The U.S. GOVERNMENT

IS ABSOLVED

FROM ANY LITIGATION WHICH MAY ENSUE FROM THE CONTRACTORS INFRINGING ON THE FOREIGN PATENT RIGHTS WHICH MAY BE INVOLVED.

1630

REEL – C

1264

A.T.I.

30819

SUMMARY TECHNICAL REPORT
OF THE
NATIONAL DEFENSE RESEARCH COMMITTEE

Manuscript and illustrations for this volume were prepared for publication by the Summary Reports Group of the Columbia University Division of War Research under contract OEMsr-1131 with the Office of Scientific Research Development. This volume was printed and bound by the Columbia University Press.

Distribution of the Summary Technical Report of NDRC has been made by the War and Navy Departments. Inquires concerning the availability and distribution of the Summary Technical Report volumes and microfilmed and other reference material should be addressed to the War Department Library, Room 1A-522, The Pentagon, Washington 25, D.C., or to the Office of Naval Research, Navy Department, Attention: Reports and Documents Section, Washington 25, D.C.

Copy No.

17

This volume, like the seventy others of the Summary Technical Report of NDRC, has been written, edited, and printed under great pressure. Inevitably there are errors which have slipped past Division readers and proofreaders. There may be errors of fact not known at time of printing. The author has not been able to follow through his writing to the final page proof.
Please report errors to:

JOINT RESEARCH AND DEVELOPMENT BOARD
PROGRAMS DIVISION (STR ERRATA)
WASHINGTON 25, D.C.

A master errata sheet will be compiled from these reports and sent to recipients of the volume. Your help will make this book more useful to other readers and will [illegible] great value in preparing any revisions.

SUMMARY TECHNICAL REPORT OF DIVISION 11, NDRC

VOLUME 1

IMPROVED EQUIPMENT FOR OXYGEN PRODUCTION

OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT
VANNEVAR BUSH, DIRECTOR

NATIONAL DEFENSE RESEARCH COMMITTEE
JAMES B. CONANT, CHAIRMAN

DIVISION 11
H. M. CHADWELL, CHIEF

WASHINGTON, D.C., 1946

NATIONAL DEFENSE RESEARCH COMMITTEE

NOTES ON THE ORGANIZATION OF NDRC

The duties of the National Defense Research Committee were (1) to recommend to the Director of OSRD suitable projects and research programs on the instrumentalities of warfare, together with contract facilities for carrying out these projects and programs, and (2) to administer the technical and scientific work of the contracts. More specifically, NDRC functioned by initiating research projects on requests from the Army or the Navy, or on requests from an allied government transmitted through the Liaison Office of OSRD, or on its own considered initiative as a result of the experience of its members. Proposals prepared by the Division, Panel, or Committee for research contracts for performance of the work involved in such projects were first reviewed by NDRC, and if approved, recommended to the Director of OSRD. Upon approval of a proposal by the Director, a contract permitting maximum flexibility of scientific effort was arranged. The business aspects of the contract, including such matters as materials, clearances, vouchers, patents, priorities, legal matters, and administration of patent matters were handled by the Executive Secretary of OSRD.

Originally NDRC administered its work through five divisions, each headed by one of the NDRC members. These were:

- Division A—Armor and Ordnance
- Division B—Bombs, Fuels, Gases, & Chemical Problems
- Division C—Communication and Transportation
- Division D—Detection, Controls, and Instruments
- Division E—Patents and Inventions

In a reorganization in the fall of 1942, twenty-three administrative divisions, panels, or committees were created, each with a chief selected on the basis of his outstanding work in the particular field. The NDRC members then became a reviewing and advisory group to the Director of OSRD. The final organization was as follows:

- Division 1—Ballistic Research
- Division 2—Effects of Impact and Explosion
- Division 3—Rocket Ordnance
- Division 4—Ordnance Accessories
- Division 5—New Missiles
- Division 6—Sub-Surface Warfare
- Division 7—Fire Control
- Division 8—Explosives
- Division 9—Chemistry
- Division 10—Absorbents and Aerosols
- Division 11—Chemical Engineering
- Division 12—Transportation
- Division 13—Electrical Communication
- Division 14—Radar
- Division 15—Radio Coordination
- Division 16—Optics and Camouflage
- Division 17—Physics
- Division 18—War Metallurgy
- Division 19—Miscellaneous
- Applied Mathematics Panel
- Applied Psychology Panel
- Committee on Propagation
- Tropical Deterioration Administrative Committee

NDRC FOREWORD

As events of the years preceding 1940 revealed more and more clearly the seriousness of the world situation, many scientists in this country came to realize the need of organizing scientific research for service in a national emergency. Recommendations which they made to the White House were given careful and sympathetic attention, and as a result the National Defense Research Committee [NDRC] was formed by Executive Order of the President in the summer of 1940. The members of NDRC, appointed by the President, were instructed to supplement the work of the Army and the Navy in the development of the instrumentalities of war. A year later, upon the establishment of the Office of Scientific Research and Development [OSRD], NDRC became one of its units.

The Summary Technical Report of NDRC is a conscientious effort on the part of NDRC to summarize and evaluate its work and to present it in a useful and permanent form. It comprises some seventy volumes broken into groups corresponding to the NDRC Divisions, Panels, and Committees.

The Summary Technical Report of each Division, Panel, or Committee is an integral survey of the work of that group. The first volume of each group's report contains a summary of the report, stating the problems presented and the philosophy of attacking them, and summarizing the results of the research, development, and training activities undertaken. Some volumes may be "state of the art" treatises covering subjects to which various research groups have contributed information. Others may contain descriptions of devices developed in the laboratories. A master index of all these divisional, panel, and committee reports which together constitute the Summary Technical Report of NDRC is contained in a separate volume, which also includes the index of a microfilm record of pertinent technical laboratory reports and reference material.

Some of the NDRC-sponsored researches which had been declassified by the end of 1945 were of sufficient popular interest that it was found desirable to report them in the form of monographs, such as the series on radar by Division 14 and the monograph on sampling inspection by the Applied Mathematics Panel. Since the material treated in them is not duplicated in the Summary Technical Report of NDRC, the monographs are an important part of the story of these aspects of NDRC research.

In contrast to the information on radar, which is of widespread interest and much of which is released to the public, the research on subsurface warfare is largely classified and is of general interest to a more restricted group. As a consequence, the report of Division 6 is found almost entirely in its Summary Technical Report, which runs to 23 volumes. The extent of the work of a division cannot therefore be judged solely by the number of volumes devoted to it in the Summary Technical Report of NDRC: account must be taken of the monographs and available reports published elsewhere.

One can claim on behalf of Division 11 that the results of its work contributed directly and dramatically to the successful prosecution and triumphant termination of World War II. It was Division 11, under the leadership first of R. P. Russell, then E. P. Stevenson, and later H. M. Chadwell, which developed the incendiary bombs with which Japan's industrial plants were reduced to ashes. Filled with jellied gasoline, the AN-M69 incendiary was credited with the highest efficiency of any bomb against Japanese factories and dwellings. More than 40,000 tons of AN-M69 bombs were dropped on Japanese cities.

Division 11 likewise applied the use of thickened fuels to portable and mechanized flame throwers, which were employed with great success against the enemy in the Pacific. Other sections of the Division did important work in developing improved techniques for the production of oxygen for military uses, and in solving numerous other problems in the field of chemical engineering, one of the most valuable contributions being the development of new hydraulic fluids.

This Summary Technical Report of Division 11, prepared under the direction of the Division Chief and authorized by him for publication, describes the activities of the Division and its contractors. It stands as a testimonial to the imagination and resourcefulness of American scientists and industrial engineers and as a record of wartime accomplishment worthy of grateful recognition.

Vannevar Bush, Director
Office of Scientific Research and Development

J. B. Conant, Chairman
National Defense Research Committee

FOREWORD

For administrative purposes and because of the diverse nature of the problems studied by Division 11 (Chemical Engineering) of NDRC, three independent sections were created: Section 11.1 (Oxygen Problems); Section 11.2 (Miscellaneous Chemical Engineering Problems), and Section 11.3 (Fire Warfare). The work of each of the three sections is presented in an individual volume of the Summary Technical Report.

The work of Section 11.1 had to do primarily with the production and use of oxygen. The oxygen program was extensive and covered the interests of the three Services—Navy, Army, and Air Forces. This work was carried out under the direction of R. P. Russell (January and February 1943), E. P. Stevenson (March 1943 to February 1945), and Dr. H. M. Chadwell (March 1945 to termination) as Chiefs of Division 11 for the periods indicated, and of E. P. Stevenson (October 1940 to March 1943) and Dr. J. H. Rushton (June 1943 to termination) as Chiefs of Section 11.1. Assisting them were Dr. C. C. Furnas as Chief Technical Aide, and Dr. S. S. Prentiss and D. Churchill, Jr., as Technical Aides of Section 11.1.

In the fall of 1940 a long-range project was initiated which required the use of large quantities of liquid oxygen as a secondary fuel for underwater propulsion of submarines. The project called for a means to generate oxygen at sea when the submarine was surfaced, and this posed an extreme problem in design of liquid-oxygen producing equipment.

Soon after work was started on oxygen for submarine propulsion, an interservice committee was set up to coordinate the oxygen needs of all Services. The Army Corps of Engineers had a need for lightweight field generating units to supply medical and repair facilities. The Army Air Forces projected large requirements for field generation of high-purity oxygen for aviation breathing purposes. Such field units were to be airborne, truck, or skid mounted, and were to be used in flight and at advanced bases. The Navy Bureau of Aeronautics had similar requirements, and the Navy Bureau of Ships needed plants for production of oxygen for repair purposes on shipboard.

Problems closely associated with the use of oxygen, such as removal of carbon dioxide from a submarine atmosphere, and the disposal of the exhaust gases from oil-oxygen fired Diesel or gas turbines in submarines, were also handled and working models were built.

The oxygen program not only involved the design of complete generating plants, but also the development of vaporizers whereby liquid oxygen could be converted to gaseous oxygen for breathing and other purposes. In addition special methods of analysis were developed for oxygen and moisture content of gases.

A large number of research and development contracts were entered into with universities and industrial organizations to develop processes and equipment to meet the specific needs of the interested Services. The Army Air Forces, the Navy Bureau of Ships, the Navy Bureau of Aeronautics, and the Liaison Officers assigned to the various projects by these Services furnished invaluable assistance without which the program could not have been effective. Standard-type industrial processes and equipment for the generation of oxygen were not suitable for military needs for field generation, and development was entered into on all component parts of oxygen-generating equipment. New methods were developed for oxygen production by both chemical and through liquefaction and distillation of air. The Summary Technical Report covers the detailed work of the section and points out the significant results.

The manuscript for this volume was prepared by Dr. Rushton and Dr. Prentiss. The coordination within the Division was supervised first by Dr. Prentiss and later by D. Churchill, Jr. To all of these men the Division Chief wishes to express his sincere thanks.

The Division Chief also wishes to acknowledge with thanks the valuable help and guidance in broad phases of the program and policy of Dr. Roger Adams, Member of the NDRC.

H. M. Chadwell
Chief, Division 11

J. H. Rushton
Chief, Section 11.1

CONTENTS

Chapter 1

INTRODUCTION

By S. S. Prentiss[a]

The activities of Section 11.1 have been concerned primarily with such means for generating and using oxygen as would be of interest to the military. There are three categories into which methods for generating and using oxygen may be broken down, namely, (1) the development of compact, lightweight, portable units for separating oxygen from air, (2) the development of equipment for supplying oxygen for specialized uses, such as aircraft breathing, and the development of instruments for testing oxygen intended for the specialized uses, (3) the generation of oxygen aboard submarines for use as a secondary fuel and the operation of internal combustion engines while the vessels are submerged.

At the start of the war the supply of oxygen on foreign battle fronts was limited to that which could be transported as compressed gas in steel cylinders. It was believed that portable generators might be developed to supply oxygen directly for a number of uses. Some manufacturers had already developed portable generators, but much remained to be done to reduce the weight and bulk of these generators and, at the same time, to increase the efficiency and convenience of operation of such units at advance bases. Improvements were sought in methods based upon fractionation of air and chemical absorbents for atmospheric oxygen.

Section 11.1 made a detailed survey of liquid air cycles and equipment for the separation of atmospheric oxygen, and decided to develop several alternative forms of apparatus for generating oxygen and charging cylinders at advance bases. The choice of the cycles and the direction which the development took was dictated by (1) expected military advantages of certain types of apparatus, and (2) availability of equipment or successful development of more appropriate machinery. Since it was difficult to weigh these factors in advance of experimental work, it was decided to build several units embodying competing ideas. The Linde system utilizing high-pressure air was attractive because of the small size and simplicity of high-pressure equipment. Low-pressure systems were attractive because they offered a means for eliminating chemicals for air cleanup, and because they used more reliable low-pressure compressors which might also prove to be space saving.

An effort was made to develop a small unit that might be operated directly upon large aircraft to give a supply of breathing oxygen to the crew, and replace thereby the cylinders of compressed oxygen which are normally carried. Although no aircraft unit was developed that compared favorably with cylinder oxygen, considerable success was had in developing a small unit for ground operation which was extremely compact and lightweight.

A unit was developed for operation with air compressor equipment available on submarines, which might be operated for brief periods, while the submarine is surfaced, to generate a supply of liquid oxygen subsequently to be used to replenish the oxygen of the atmosphere in order to prolong periods of submergence. Some of the features of this unit made it attractive for a trailer-mounted generator.

Some of the generators previously mentioned were redesigned to permit transportation by air and operation at air bases. Still others were redesigned for operation on shipboard.

A requirement of the Navy for a fuel oxygen on submarines led to the development of a unit of extreme compactness for the generation of large quantities of liquid oxygen aboard submarines. Oxygen was to be generated while the submarine was surfaced, and used as a secondary fuel in internal combustion engines for submerged operations. Two types of units were developed in pilot-plant size, each producing approximately 400 pounds of liquid oxygen per hour. The first of these operated with low-pressure air, giving a unit which could operate with the most compact type of centrifugal air compressors. A second unit using medium-pressure air supply was operated but was found to be less advantageous.

Much effort was devoted to detailed study of types of equipment applicable to the specialized requirements of the different units. Air compressors and expansion engines normally used in commercial plants and available on the market were all low-

[a] Technical Aide, Division 11, NDRC.

speed, extremely heavy and bulky, and thus not easily adapted to portable units. High-speed air compressors were developed from aircraft engine chassis, resulting in compactness and lightweight which were essential for portability. Improved expansion engines were developed which would operate at extremely low temperatures without lubricants.

A lightweight oxygen compressor was also developed which could be used without water lubrication and thus avoid the necessity of redrying oxygen after compression.

Liquid oxygen pumps were developed which, when associated with suitable heat exchanger equipment, could be used to charge high-pressure cylinders directly from liquid oxygen. One type could be associated with the rectification column and heat exchanger of an oxygen-generating unit for delivery of the oxygen product at a pressure suitable for charging cylinders. A second type operated manually with an external supply of liquid oxygen.

Heat exchanger equipment of both exchanger and regenerator (heat reservoir) types was critically studied and developed. The most important was a multi-pass construction suited for the deposition of water vapor and carbon dioxide, which combines the functions of exchanging heat between the different streams of gases in the system and removing condensable impurities from the air stream. This is brought about by periodically alternating the gas streams between two or more channels in the heat exchanger, so that the impurities condensed from the incoming air will be re-evaporated and removed by the effluent nitrogen.

In all of the generating units under consideration, a limitation was placed on the height of the fractionation column necessitating the development of columns with a high efficiency per unit of height. Columns of both the tray type and the packing type were studied. For units to be used on shipboard there was a further requirement that trays should give results independent of the pitching and rolling of the vessel. Several approaches were made to the problem: (1) transverse baffles were inserted in bubble cap trays, (2) the packing of the column was caused to rotate slowly, thus avoiding not only the effects of roll and pitch but also any permanent deflection of the column from the vertical, (3) special packings were designed to distribute reflux liquid, and (4) further improvements were made in the efficiency of the column for unit height, providing sufficient margin of operation.

A study was made of the injurious effects upon oxygen-generating equipment, of water vapor, carbon dioxide, and combustible impurities from air, and of the means for their removal. These include the use of caustic absorbents, such as potassium hydroxide, Sodalime, Barylyme, and of other products recently placed on the market, the use of regenerable absorbents such as activated carbon and activated alumina, the deposition of the impurities on cold surfaces as described above under heat exchangers, and the filtration of impurities from liquid air streams.

In addition to the development of mechanical means, the possibility was examined of a unit based on organic chelate compounds known experimentally to be capable of reversibly absorbing atmospheric oxygen. A large-scale source of this material was developed, and portable units for separating oxygen from the atmosphere were designed. It was soon found that truck-mounted chemical units could not compete with the liquefaction units in weight and fuel requirements. A unit of this type for operation on shipboard was, however, developed and tested extensively for cutting and welding oxygen supply.

Several systems for generating oxygen from chemicals were studied. An apparatus was developed for generating oxygen from sodium peroxide and potassium tetroxide on a demand basis, suitable for use in the field for cutting and welding operations, medical therapy, etc. In association with other groups, Section 11.1 developed a sodium chlorate composition, possessing good storage characteristics, and an apparatus for supplying breathing oxygen, for emergency use on aircraft, to be operated with standard demand mask equipment. Improvements were also made in "rebreathers" for aircraft, making them available for emergency use at low temperature; these rebreathers combine potassium tetroxide as a rebreather agent with sodium chlorate composition as a priming agent.

For full utilization of savings in weight and volume, a system for storing oxygen as liquid rather than as compressed gas was developed together with means for converting the liquid to gaseous oxygen when necessary for use on aircraft, in medical therapy, and in engineering applications. Most attention was given to the development of large liquid oxygen vaporizers, for use on bombers and transport aircraft, to supply crew members and other personnel with breathing oxygen. Small individual units for walk-around use were also developed which compared very favorably with compressed gas systems.

An instrument was developed for determining the partial pressure of oxygen in a mixture of gases. It had a number of other uses, including that of determining the purity of generated oxygen, the percentage of oxygen in breathing gases such as are used at high altitudes, in medical therapy, and on submarines, and the concentration of oxygen mixed with combustible gases.

Water vapor in concentrations of more than 0.02 mg/l in oxygen intended for aviation use constitutes a sufficient hazard at low temperature to make it desirable to determine the moisture content of large numbers of cylinders. A simple, convenient test which required but a small gas sample was devised. This led to refinements in the frost point method and to the development of a chemical indicator based on color change. The frost point apparatus seemed to solve this problem satisfactorily, but the chemical methods were never developed sufficiently, in point of view of reproducibility and storage characteristics, to be useful as a procedure for field instrument operation.

A combined vapor pressure and gas thermometer was developed to cover the entire range from ambient temperatures to the boiling point of oxygen.

A detailed study was made of the operation of diesel engines on closed cycles (under submerged conditions) with dilution of the combustible agents of fuel and oxygen with exhaust gases rather than atmospheric nitrogen. There was, further, the problem of disposing of exhaust gases from a submerged submarine, in such a way that it would not appreciably contribute to the vessel's being visibly detected. Means were developed for dispersing the exhaust gas as very fine gas clouds which would be quickly dissolved in sea water.

Chapter 2

OXYGEN

By *J. H. Rushton*

2.1 CYCLES AND EQUIPMENT FOR THE MECHANICAL SEPARATION OF OXYGEN FROM AIR

2.1.1 Oxygen Production Units for Military Purposes

In the latter part of 1941 it became apparent that there was a military need for equipment to produce oxygen on naval vessels and at advanced military land bases. Military requirements were summarized at a meeting in January, 1942.[1] The Navy suggested three types of plants for oxygen production.

1. A unit to be operated on shipboard to produce approximately 600 cfh of high purity oxygen deliverable at about 150 psi for use in cutting and welding.

2. A plant for the production of up to two tons of 95% liquid oxygen per hour. This large plant was to be developed from a smaller pilot plant built to obtain necessary engineering information. The immediate interest was therefore centered in a pilot plant for the production of about 400 pounds of 95% liquid oxygen per hour.

3. A small liquid oxygen plant to supply breathing oxygen for submarine use. This plant to produce about 35 lb of liquid oxygen per hour at purity of at least 95%.

The Army was interested in three other types of plants for oxygen production.

1. A mobile gaseous oxygen plant to produce 1,000 cfh of high purity (99.5%) oxygen for breathing purposes. This oxygen to be compressed to about 2,000 psi.

2. A unit transportable by air with a capacity of at least 400 cfh of breathing oxygen compressed to 2,000 psi.

3. An airborne unit to operate in a plane while in flight, to have a capacity of about 120 cfh (standard temperature and pressure) of high purity breathing oxygen for delivery at pressures above 10 psi.

In 1942 the Army had available for procurement large trailer plants weighing approximately 34,000 lb which could be used for mobile oxygen supply. The Navy had nothing in sight to fulfill their requirements. Accordingly, the NDRC program was extended in scope to try to fulfill all the requirements of the Services.

A complete survey was made of the many proposed cycles for the production of oxygen from air. This section of the report concerns those cycles which are primarily mechanical in operation. They all involve the compression of air, its liquefaction, followed by rectification, and, finally, by compression of the resulting oxygen. Other means for producing oxygen to satisfy military requirements are covered in Chapters 11 and 12.

2.2 TYPES OF CYCLES

Fundamentally there are only two types of cycles in use: the Linde and the Claude cycles, but there are many variants of these.

2.2.1 The Linde Cycle

This cycle is illustrated diagrammatically in Figure 1. The high-pressure air is cooled by heat exchange with the outgoing streams of oxygen and waste nitrogen, expanded through a valve to an intermediate pressure, condensed in the reboiler of the tower by the boiling oxygen, throttled to the tower pressure, and introduced to the tower as liquid reflux. The refrigeration is supplied in the cooler, and the cooling obtained by the large temperature drop which accompanies the expansion through the first valve. Often this system is supplemented by a low-level refrigeration, or forecooling step before expansion of the high-pressure air. In this cycle the head pressure is maintained at least as high as 600 to 700 psi, and frequently as high as 3,000 psi.

2.2.2 The Claude Cycle

This cycle is also illustrated in Figure 1. In this system the refrigeration is supplied by allowing the air to do work in an expansion engine. The air pressure used may vary from 60 psi to 3,000 psi. When the head pressure is low, as in the M-7 unit, the air after expansion in the engine is at such a low pressure that it cannot be condensed by the boiling oxygen and is therefore not available as liquid reflux. This expanded air may either be returned immediately to the heat exchanger, or it may be used to aid the fractionation process, as shown in the sketch. There is also a variation of this cycle in which the expansion is to a pressure high enough so that the exhaust may be condensed and used as liquid reflux.

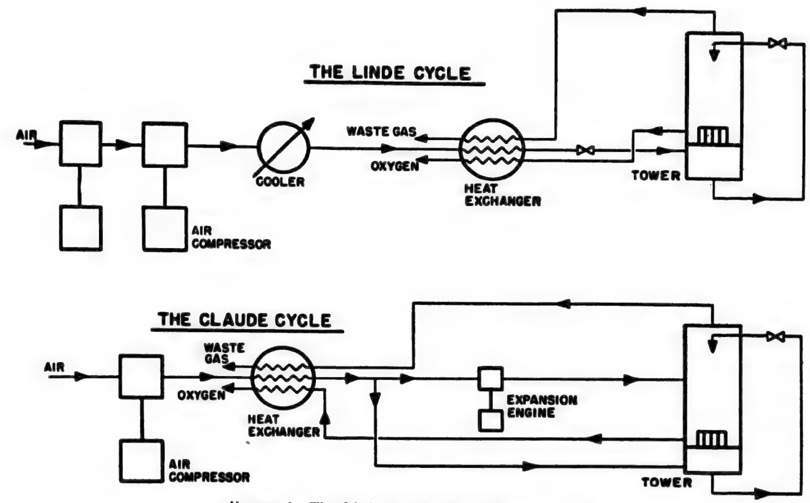


Figure 1. The Linde cycle and the Claude cycle.

2.2.3 Other Cycles

Exhaustive study was made of a number of modifications of the two cycles shown in Figure 1 to evaluate relative advantages and possibilities. Ten rather distinctive variations are shown in Figures 2 to 11 and they cover the basic processes to which practically all known mechanical cycles for oxygen production are related. Each figure is labeled to show the particular characteristic of the cycle. Complete thermodynamic analyses were made, and engineering considerations necessary to build plants on a reasonably large scale were studied. In particular, the size and weight of compressors, expanders, air clean-up systems for the removal of carbon dioxide, dryers, heat exchangers, and rectifying columns were carefully investigated. On the basis of these summaries and refrigeration requirements, certain cycles were found to offer great advantages in compactness and ease of air clean-up, providing suitable compression equipment could be made available. These studies were summarized in reports which give complete details on the methods of calculation used.[2,3,4,7,8]

Military requirements indicated the need for both very small and very large plants. The small plants were to be as light in weight as possible, of minimum height and to require small floor space and volume, at the expense (if necessary) of high fuel economy. The smallest plants were to be very easily transportable, but larger plants of approximately 1,000 cfh were to be capable of installation on lightweight trailers. The large stationary plants were to have moderate weight with small floor space and were to require very low power consumption. For all plants it was felt that great emphasis should be placed upon simplicity of operation and the elimination, so far as possible, of chemical supplies for the removal of carbon dioxide and water from the air to be processed.

An examination of equipment weights and sizes necessary for small oxygen production plants showed that there was great room for improvement in essential items, such as compressors and air clean-up equipment; that development of lightweight units

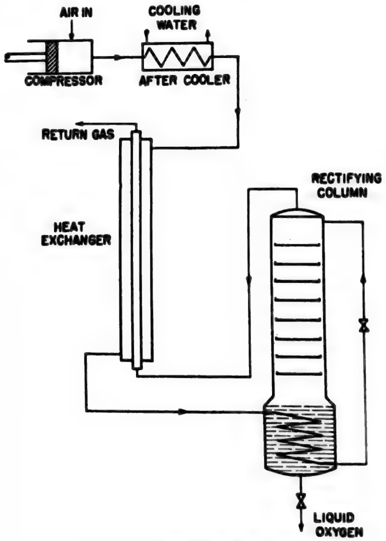


FIGURE 2. Joule-Thomson cooling.

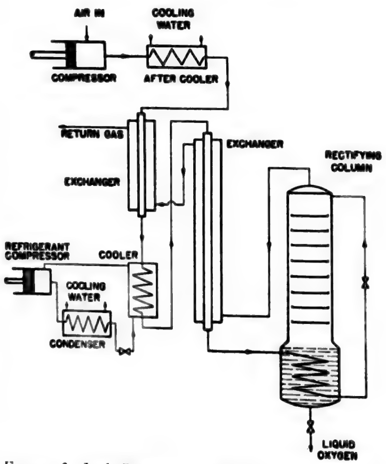


FIGURE 3. Joule-Thomson cooling with auxiliary refrigeration.

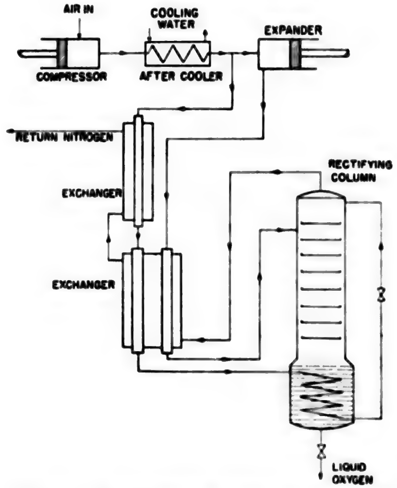


FIGURE 4. Joule-Thomson cooling and expansion engine with high temperature intake.

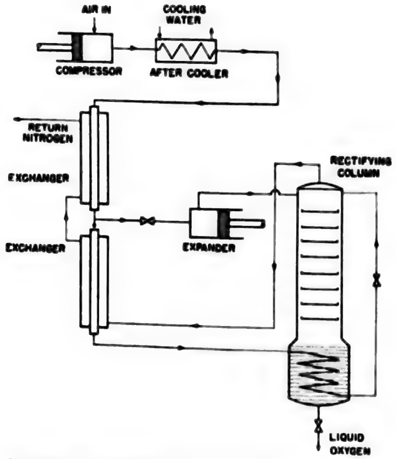


FIGURE 5. Joule-Thomson cooling and expansion engine with low temperature intake.

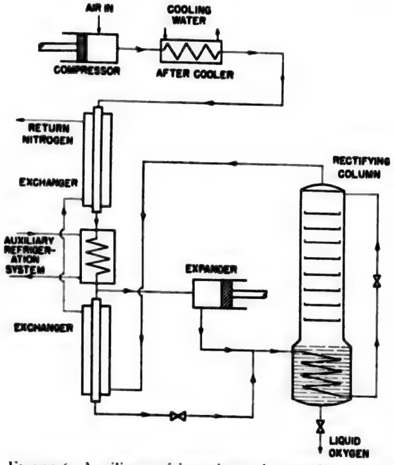


FIGURE 6. Auxiliary refrigeration and expansion engine combined.

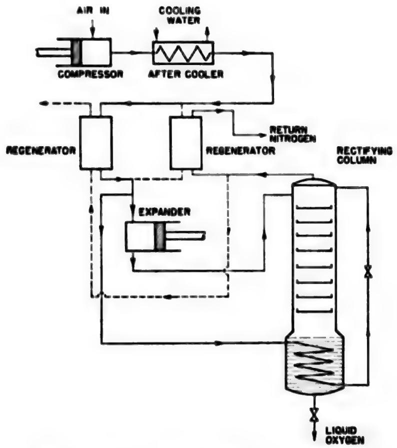


FIGURE 7. Expansion engine with low temperature intake regenerative heat exchangers.

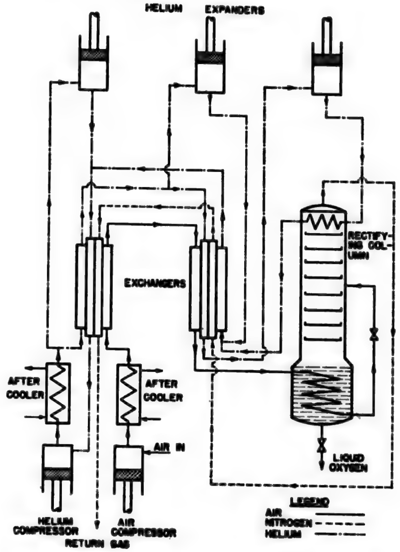


FIGURE 8. Refrigeration by three-stage helium expansion.

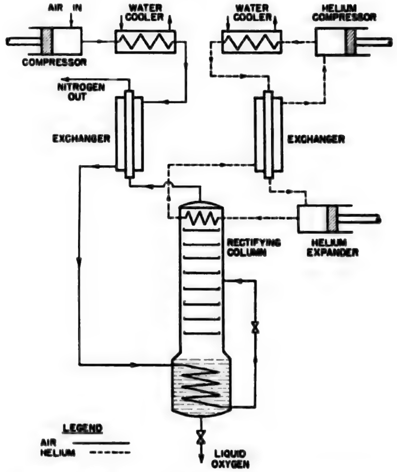


FIGURE 9. Single-stage helium expansion refrigeration applied to column.

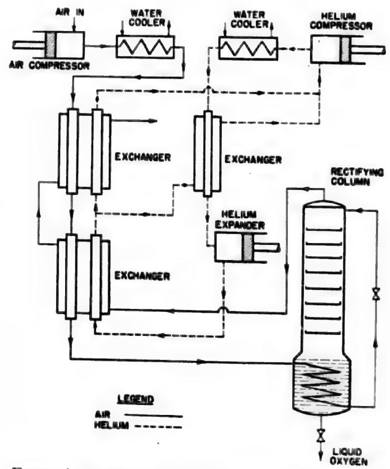


FIGURE 10. Single-stage helium expansion refrigeration applied to exchanger.

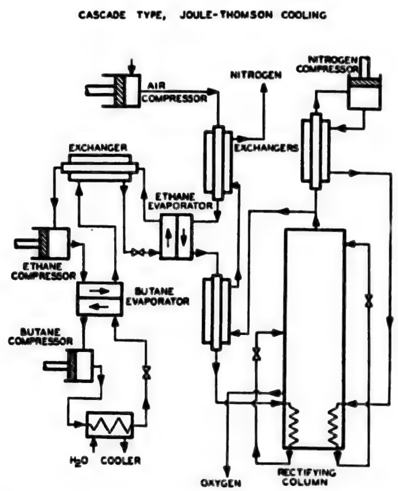


FIGURE 11. Expansion engine with low temperature intake recuperative heat exchangers.

would probably be feasible, and that research and mechanical development to this end could be justified.[4]

The cycles of greatest potential value to the services were grouped into those involving low-pressure air supply (up to 150 psi) and those involving intermediate (600 psi) and high-pressure (up to 3,000 psi) air supply. In all cases, equipment for the component parts of the cycles were evaluated with regard to procurability, operating characteristics, and weight. For almost every item of equipment a program of research and development was initiated to produce the lightest and most compact unit.[5,6] Individual types of equipment such as compressors, heat exchangers, etc., will be described under separate headings and will follow a description of the cycles and units which seemed to offer the best possibilities for achieving the military requirements.

2.3 EQUIPMENT DEVELOPED IN THE OXYGEN PROGRAM

In Chapters 3 and 4 several cycles for the mechanical separation of oxygen from air are discussed, and operating units are described together with details as to size and operating characteristics. Since military requirements emphasized the need for compactness, simplicity, lightness in weight and minimum height, together with dependability and ease of maintenance but not necessarily coupled with the high efficiency required in industrial operations, it was necessary to investigate the design of all component parts of equipment used in the separation of oxygen from air by mechanical means. To obtain the desired compactness and mobility it was necessary to investigate the possibility of developing very lightweight equipment. Further, the thermodynamic efficiency of the component parts had to be as high as possible. In so far as possible the aim was to develop equipment which would require an absolute minimum of chemical supplies other than fuel and lubricants. Plants were developed and built which used other chemical supplies but the reasons for this were twofold: First, because the use of chemicals for air cleanup was a customary operation, and its success was assured. Therefore, cycles were used depending upon chemical cleanup so that there would be a greater chance of developing a useful unit if the other processes, wherein chemicals were not required, should prove to be failures. Second, it might well develop that processes in which chemicals were not required for air clean-up would become too complicated and too sensitive in operation for successful military application and that it might, in the end, become more practicable to set up a service supply of chemicals than to have less dependable equipment in the field.

There are a number of operations which are the same in all the processes mentioned before. For example, air compressors, heat exchangers, reboilers, and fractionating columns are common to all mechanical processes. A study was made of the equipment available for each of the operations for all of the cycles investigated. As a result it was decided to initiate experimentation and development on the performance and construction of most of the component parts of the plants under consideration. Considerable success was achieved in the development of compact lightweight equipment. A great deal of information has been obtained on the performance of various types of heat exchangers and fractionating columns. Considerable experimental data have been obtained on the thermodynamic properties of air and the impurities in air such as carbon dioxide and acetylene, and these data have already been made use of in the development of plants, and will, no doubt, be of considerable use in the future. The great amount of experimental data and equipment development will be summarized briefly in the following chapters.

Chapter 3

LOW-PRESSURE CYCLES AND UNITS

By *J. H. Rushton*

3.1 THE COLLINS AIRBORNE UNIT

Cycles for oxygen production operating at low pressure offered great possibilities for the use of compact lightweight equipment. A very small unit had been operated experimentally, using air at 150 psi, corresponding in general principles to the cycle in Figure 5, Chapter 2. This unit, proposed by S. C. Collins,[1,4] had the distinct advantage of being able streams, but is also used as a mechanism for precipitating water, ice, carbon dioxide, and hydrocarbons from air. These impurities are then evaporated into the effluent nitrogen stream on suitable reversal of gas flows. The use of such heat exchangers offers the possibility of eliminating chemical clean-up supplies, and, if successful, would reduce the complexity of equipment of the oxygen plant. Previous to the operation of the Collins unit, the Linde-Fränkl cycle

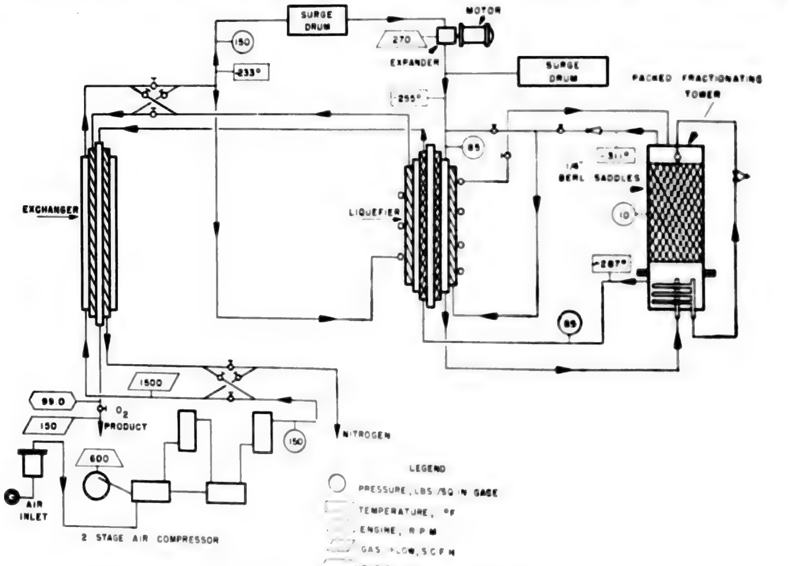


Figure 1. [illegible] 150 cfh (Collins).

to operate without the use of chemical agents [illegible] removal of carbon dioxide, [illegible] compressed air. [illegible] as originally [illegible] most arresting [illegible] changer.[2] The [illegible] transfer heat [illegible] had been operated with considerable success in large [illegible] in Germany. In the Linde-Fränkl cycle, regenerators were used in place of heat exchangers. [illegible] water, carbon dioxide, et cetera, were deposited [illegible] these regenerators. The precipitated water, [illegible] dioxide, et cetera, were then evaporated by [illegible] nitrogen to which was added an additional

air stream, and which, processed at high pressure, had been dried and cleaned by the use of chemicals. This additional stream, together with the effluent nitrogen, was sufficient to cleanse the regenerators and allowed the cycle to operate. The Collins heat exchangers offered the possibility of eliminating the use of the extra air stream and all the equipment and supplies necessary for its proper functioning.[8] Further, the Linde-Fränkl cycle had been operated at low pressures (usually around 90 psia but on occasion as low as 45 psia) and it appeared feasible that lightweight compressors could be obtained of both reciprocating and rotary design for portable oxygen plants if pressures in the neighborhood of 100 psia could be proved useful for military oxygen production. Both the Collins and the Linde-Fränkl cycles made use of a low-temperature expansion engine. The Kapitza-type centrifugal expander was rumored to have been used in Linde-Fränkl plants in Germany, and small reciprocating expanders were available in the United States. One of the features of the Collins unit was its ringless piston expander which provided complete refrigeration for the unit.[3,5] It was largely upon the considerations just mentioned that model plants were built embodying features of the low-pressure and Collins cycles.

Final development of the Collins cycle and unit is illustrated in Figure 2, which shows the final flow sheet for the production model, and Figure 3, which shows the unit before insulation and without air and oxygen compressors. The unit has been produced in quantity for both the Army Air Forces and the Navy.[5] The unit requires 25 scf per min of air at 150 psi and produces 99.5+% gaseous oxygen at a rate of 150 cu ft per hr. The unit, without air and oxygen compressors, weighs 165 lb and occupies a volume of approximately 9 cu ft.

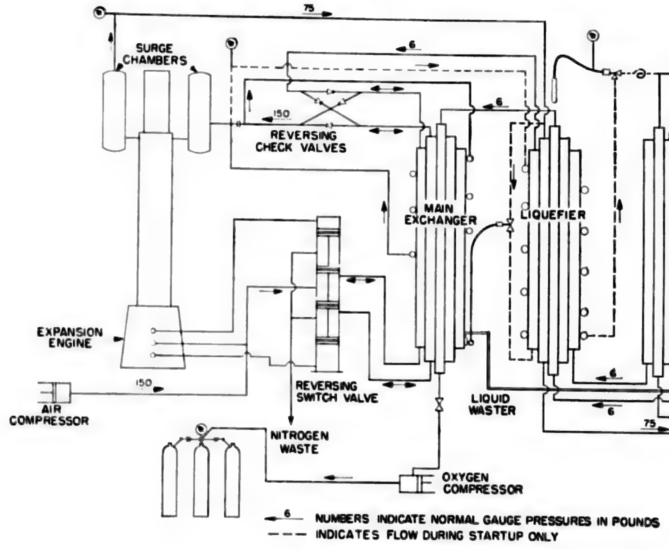


Figure 2. Collins final unit.

3.2 MOBILE LOW-PRESSURE GASEOUS OXYGEN UNITS

3.2.1 Kellogg M-2 Plant

Two lines of development were followed to develop a mobile 1,000 cfh high-purity gaseous oxygen unit. Plans were laid out for both a low-pressure

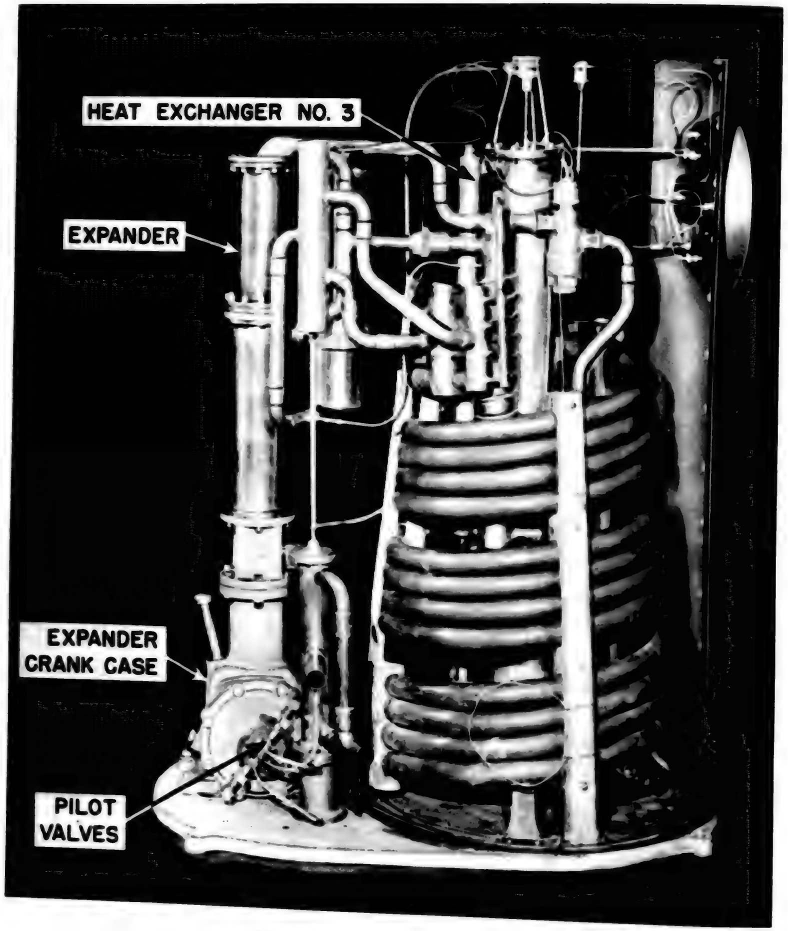


FIGURE 3. Aircraft oxygen generator.

and a high-pressure [illegible] M-1. The low-pressure plant was to be [illegible] using regenerators together with [illegible] and to operate with air pressure [illegible]. This was designated as the M-2 unit and the flow sheet for it is shown in Figure 4. The unit was operated briefly but not very successfully due to equipment failures. It is now believed that the cycle of Figure 4 would not

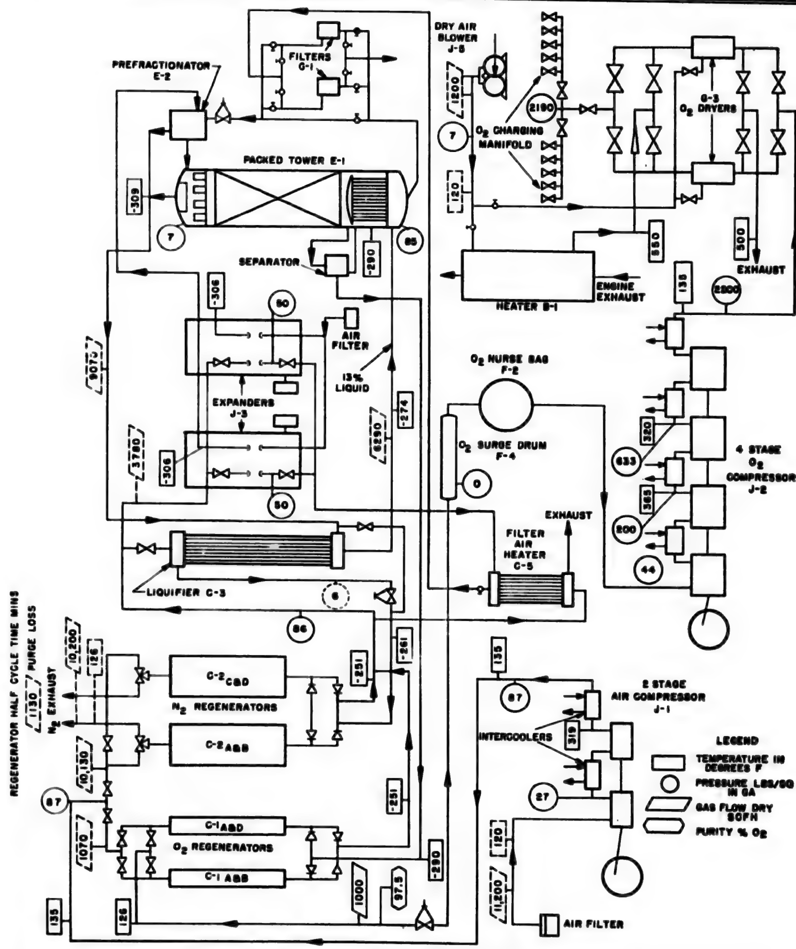


FIGURE 4. M. W. Kellogg Co. design conditions for 1,000 cfh mobile oxygen unit, LP system unit M-2.

allow continuous operation for extended periods of time. Slight modification of the cycle to allow proper cold-end temperature approach at the regenerators would probably make the cycle operable. Plans were made to test this point but the pressure of other matters has made it impossible to do so. Details regarding the action of heat exchangers and regenerators functioning as air cleaners for the removal of carbon

dioxide, water, et cetera, will be covered in later chapters. Equipment and operating details of the M-2 unit are available.[10,11]

3.2.2 Kellogg M-7 Gaseous Oxygen Plant

A cycle was laid out and a plant built based on the use of Collins reversing heat exchangers utilizing air at 105 psia.[9] The plant was designed for the production of 1,000 cfh of 99.5+% oxygen under extreme temperature and humidity conditions. All of the equipment was to be mounted on a trailer and the only supplies were to be gasoline, lubricating oil, and a small amount of water. This project was designated M-7, and held that notation through all experimental work. A number of units based on this cycle were built for the Services and for Lend-Lease.[13] Complete details of the M-7 development appear in progress and final reports; they are summarized elsewhere.[11,13] Details pertaining to the cycle are of interest because the cycle has proven to be the best for military production of gaseous oxygen, and has been modified and adapted to the production of liquid oxygen on a large scale. Also a high-capacity, lightweight, air-transportable model of the cycle has been procured by the Air Forces.[13] A general description of the M-7 plant and its process follows.

The M-7 unit was designed to produce 1,000 scfh of 99.5% gaseous oxygen under the rather extreme atmospheric conditions of 120 F ambient and 90 F dew point, and to deliver this oxygen dry (dew point —70 F) at 2,200 psi. Under more usual atmospheric conditions, such as 70 to 80 F ambient, the unit has produced 1,300 standard cfh of 99.45% oxygen, with no increase in feed air capacity. If the compressor and engine are speeded up to deliver 15% more than the designed air capacity, the unit will deliver 1,500 scf per hr of oxygen at 98.7% purity. The unit was designed to run continuously for periods of 120 hr or more.

The refrigeration required by the unit is supplied by a reciprocating expander working at a head pressure of 100 psia. Water and carbon dioxide are removed by condensation and evaporation in the reversing exchanger, and not by chemical means, thus making the unit independent of any chemical supply whatever. This is a characteristic of great importance in a field unit. A single tower with vapor feed is used for fractionation and the oxygen is compressed in a dry, non-lubricated compressor. A flow sheet with typical operating data is shown in Figure 5.

Air Compression. Atmospheric air is filtered, then compressed in a two-stage, high-speed, air-cooled reciprocating compressor, and is cooled after each stage of compression directly against cooling air, any condensate being separated out after each stage. The cooler is designed to cool the compressed air to 135 F when the ambient air is at 120 F with 90 F dew point.

In the second stage, 100 psi air, after leaving the entrainment separator, flows through a special paper filter to remove any entrained oil (down to 1 micron drop size). It is important to remove entrained oil completely, because presence of oil in the air prevents the proper purification by the exchanger.

Air Purification and Heat Exchange. The compressed, filtered air enters the parallel tubes of a reversing exchanger (Collins tubes) through a reversing valve. Each reversing exchanger tube is a three-annulus, three-fluid exchanger in which the incoming air is cooled by means of the effluent oxygen product and waste nitrogen. The two channels or passages which carry the air and waste nitrogen are very similar in size and in flow resistance, but the oxygen annulus is much smaller. The coldest section of the exchanger (fourth tube pass) has three small tubes coiled around and soldered to the exchanger, making it a four-fluid unit at this point. Part of the waste nitrogen flows continuously through these coils which are known as the "*unbalance flow*" pass. All annuli have extended surface packing and are in soldered thermal contact with each other and with the outer tube coils.

Though oxygen flows continuously through its passage, the operation of the reversing valve causes air and waste nitrogen to be diverted periodically from one of the two passages to the other, and, as a result, waste nitrogen flows at all times through a passage which had carried feed air during the previous part of the cycle. The switching of these two streams results in the purification function of the exchanger. Thus, in one half-cycle, when air is being cooled, first water ice and then carbon dioxide snow are precipitated from the air and are deposited on the metal surface. Before this process has continued to the point where the surface has become seriously fouled, the reversing valve causes the waste nitrogen to stream through the impurity-laden channel. Though the waste nitrogen is colder than the air, the fact that its total pressure is much lower enables it to evaporate the impurities which are lodged on the surface as a result of the passage of air in the pre-

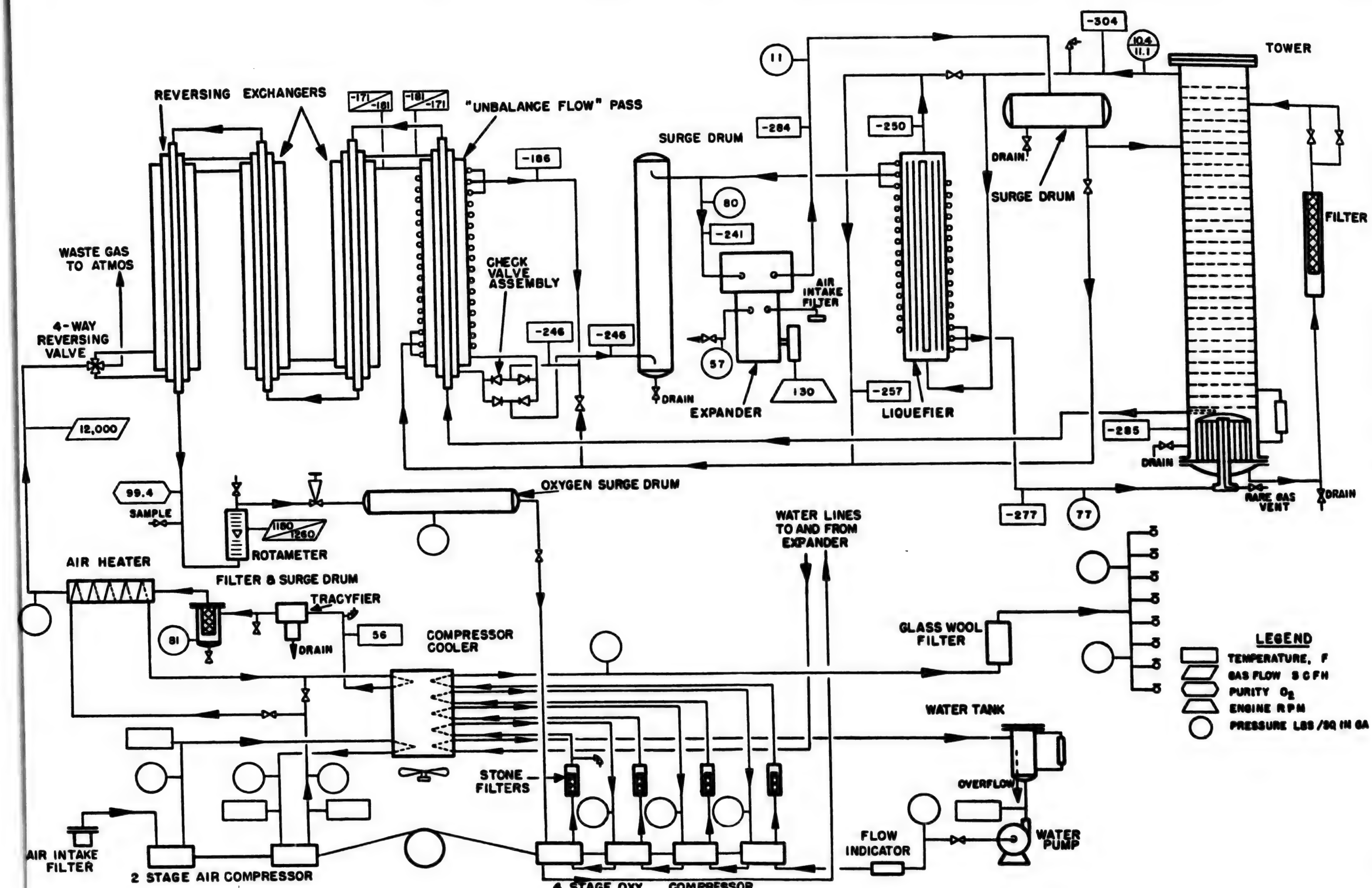


FIGURE 5. M. W. Kellogg Co. M 7 mobile oxygen unit.

vious half-cycle. The evaporated impurities are then carried out of the system by the waste nitrogen, and the unit can therefore operate continuously without chemical purification of the feed air.

The water impurities deposit at the warm end of the exchanger, where the normal relationship between pressure and temperature of the two switching streams is satisfactory for proper evaporation of the water ice. The carbon dioxide, on the other hand, precipitates at the cold end of the exchanger and in this region normal conditions of temperature and pressure do not suffice to insure evaporation of the carbon dioxide. A fourth heat exchange passage (called the unbalanced flow pass) is therefore provided in the coldest part of the exchanger. Part of the waste nitrogen flows through this fourth channel continuously before entering either one of the two reversing annuli of the reversing exchanger. By means of this continuous flow, the temperature relationships are sufficiently changed and controlled so that evaporation of carbon dioxide is satisfactory for prolonged operation.[7,8] This fourth passage consists of three parallel coils of small tubing wrapped around the coldest portion of the reversing exchanger.

Refrigeration. The purified air, after being cooled in the reversing exchanger, leaves through a system of check valves which operate in response to the reversing valve at the warm end of the exchanger. From the check valve manifold the feed air flows to a high-pressure surge drum, and from the surge drum, part of it (roughly 23%) flows to the expander where it performs external work and generates all the refrigeration required by the plant. The expanded air flows through a second surge drum and then to the tower as vapor feed, below the sixth tray.

The remainder of the air from the high-pressure surge drum (about 75%) flows to the liquefier exchanger, which is a two-fluid, steady flow exchanger, where it is further cooled and partially condensed. This portion of air then enters the condenser in the tower reboiler where it is condensed to liquid. It is then filtered through a glass cloth filter and throttled into the tower as reflux below the first tray from the top.

Fractionation System. The fractionation tower consists of a single column fed with liquid air and with expanded air (vapor feed). A single column requires considerably less height than a double column, and low height has been a controlling military requirement. The expander discharge, at a pressure too low to be condensed in the reboiler of the tower, is fed to an intermediate point of the column as vapor. Low-pressure air cannot be condensed in the reboiler nor be fractionated by itself; however, the introduction of the vapor feed to the low-pressure tower is beneficial, because it allows a greater recovery of oxygen from the high-pressure liquid feed than is theoretically possible in a simple single column without vapor feed. Thus the advantage of vapor feed is that single-column performance can be surpassed, and double-column performance approached while maintaining the simplicity of a single liquid expansion valve.

The tower has a dry tray at the top as an entrainment separator, and a special oxygen draw-off tube below the bottom tray to minimize entrainment in the oxygen below the bottom tray.

Most of the waste nitrogen overhead flows through the liquefier exchanger, and the remainder through the fourth channel at the cold end of the reversing exchanger, and then through the check valves into the reversing exchanger and out of the reversing exchanger through the reversing valve to the atmosphere.

The oxygen, after leaving the tower, flows through the reversing exchanger, by-passing the liquefier. Since oxygen flows continuously through its annulus, which is not contaminated by air, water, or carbon dioxide, the oxygen produced is pure and dry.

Oxygen Compression. The oxygen from the reversing exchanger flows through a surge drum into the oxygen compressor, which is a four-stage, dry, non-lubricated, water-cooled reciprocating machine. After each stage of compression the oxygen is filtered through porous stone to remove carbon dust from the rings, and is then cooled by an air-cooled heat exchanger against a blast of cooling air. The compressed oxygen is charged to cylinders at 2,200 psi as final product, and is perfectly dry and suitable for aircraft breathing since no water for lubrication of the compressor is required.

Miscellaneous. The energy of the expander is absorbed by means of a built-in, water-cooled air compressor. This water-cooling duty and the water-cooling duty for the oxygen compressor are effected directly by cooling air. Oil-cooling for the engines and compressors is supplied by air-cooled units built into the machines.

A supply of hot, clean air, for use in thawing out the plant as occasion requires, is made available by the air heater exchanger. In this unit air which has

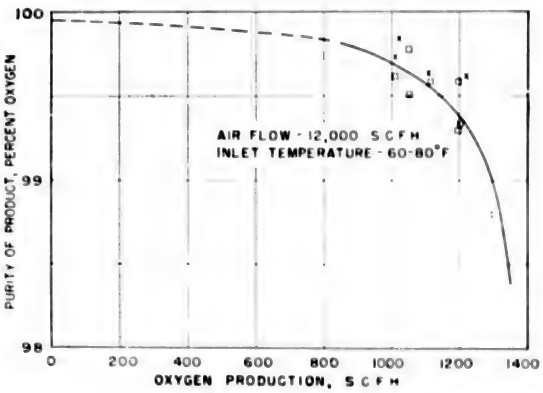


FIGURE 6. Production of M. W. Kellogg low-pressure oxygen unit M-7.

been compressed, cooled, freed of entrainment, and filtered is then heated by means of the hot air discharged from the second stage of the compressor.

Control. The M-7 low-pressure unit has five process control valves. The expander control valve CV-1 (Figure 5) is located on the brake compressor discharge line, and is manipulated in order to control the expander speed and therefore the refrigeration balance of the unit. When the liquid level tends to drop, this CV-1 valve must be opened somewhat in order to speed the expander and build back the liquid level.

The reflux valve CV-2 throttles liquid air into the top of the column, and is used to control the head pressure at which the unit operates. This is possible because the tower is equipped with a forced-feed reboiler, and when the CV-2 reflux valve is closed, liquid builds up in the condenser tubes. The consequent partial blanking of the condensing surface causes the head pressure to rise so that condensation may proceed on the smaller surface.

The unbalance control valve CV-3 is set in the waste gas line, feeding the reversing exchanger at a point between the connections to the fourth or "unbalance flow" passage at the cold end of the reversing exchanger. When this valve is closed, part of the waste gas is circulated through the unbalance coil and in this manner produces a reduction in the temperature approach between the two reversing streams, thus improving conditions for evaporation of carbon dioxide. The cold end approach is usually maintained at 5 to 8 F, and this CV-3 valve must be closed sufficiently to accomplish this.

The oxygen draw-off valve CV-4 is on the oxygen line downstream of the (warm) reversing valve, and is used to control the purity of the oxygen indirectly by controlling the total quantity of oxygen withdrawn. For maximum production, this draw-off valve is opened as much as possible without incurring a loss in purity.

The liquefier by-pass valve CV-5 is used to control the reversing exchanger outlet air temperature. As this valve is opened, colder waste gas is sent to the reversing exchanger, and thus its outlet temperature is dropped. The outlet temperature should be cold enough so that the bulk of the carbon dioxide is trapped out in the reversing exchanger, but at the same time not so cold as to produce liquefaction in the expander.

Of these five control valves, the reflux valve CV-2 is the only one that may require frequent attention, and this is probably due to partial plugs caused by residual carbon dioxide in the stream. The CV-1 expander control valve setting needs attention in order to control the liquid level should there be a change in atmospheric conditions. The remaining three valves, however, require no attention after the unit has been brought to a steady operating condition and the settings have once been made. This is reflected in the very steady operation of the unit and the complete absence of any periodic variation in pressures or temperatures in the plant. This steadiness of operating conditions is reflected in the ease with which the unit can be operated very successfully by personnel with no process or engineering background at all.

Performance Data. The gaseous oxygen production of the unit in its final form is illustrated in Figures 6 and 7. Figure 6 shows production at a total air flow of 12,000 scfh air, which was used in most tests. The general shape of the curve is drawn with some consideration for measurements taken on

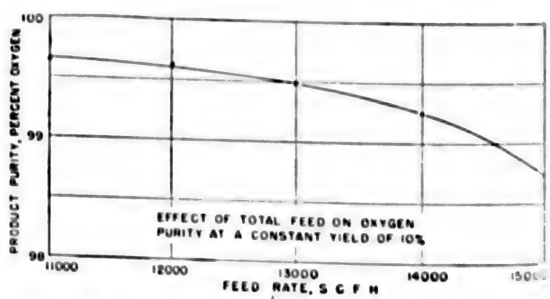


FIGURE 7. Liquid air fractionation portable oxygen unit M-7, run 22.

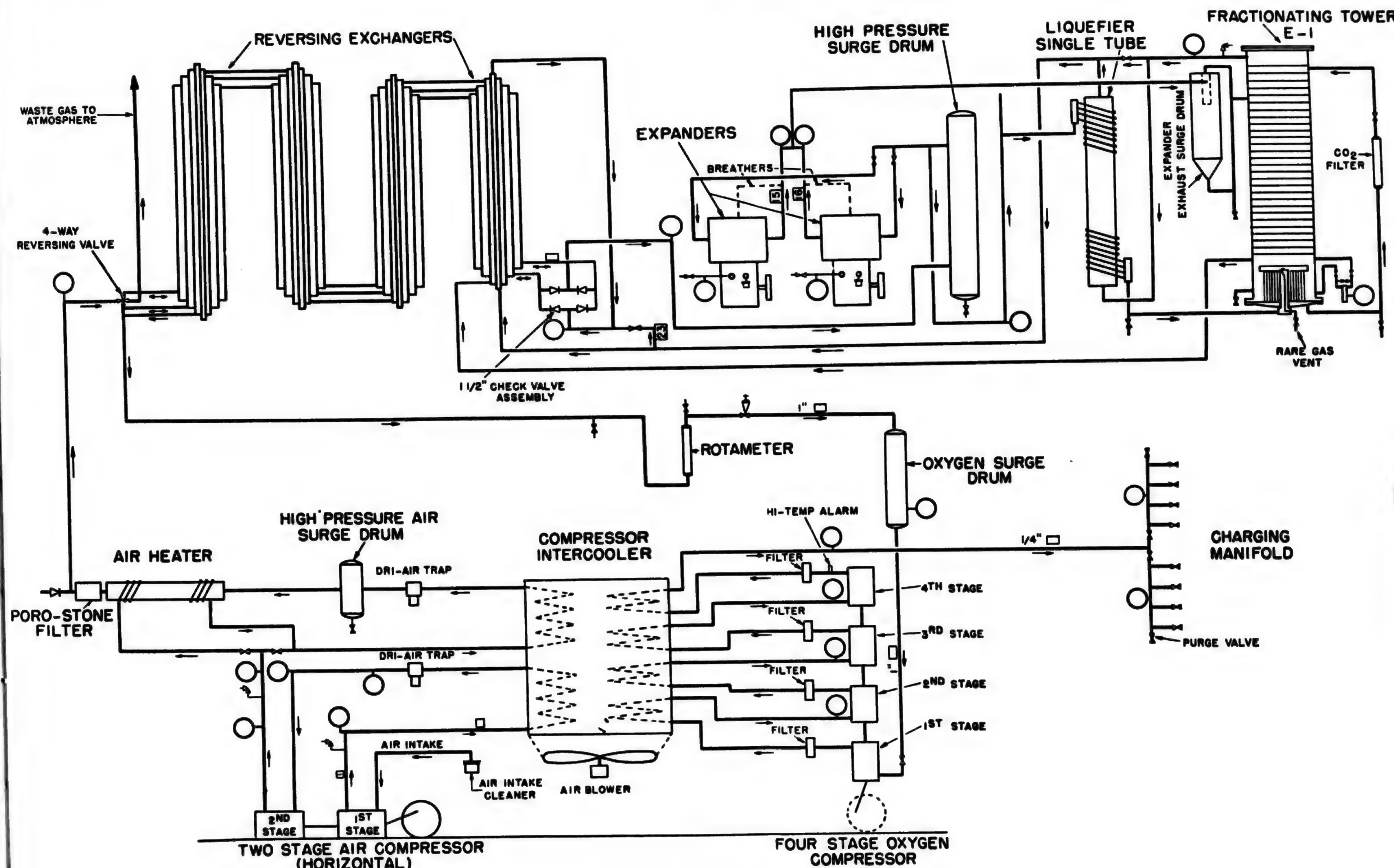


FIGURE 8. Model LP-1 flow diagram.

the unit before all the final changes were made. Figure 7 shows the effect of increasing the total air feed to the unit. The tests summarized in these two charts were made with an inlet air temperature of 60 to 80 F. The following tabulation gives the results of tests made with feed air saturated with water at 135 F (equivalent to 120 F ambient air).

The tests on the M-7 unit were made almost exclusively with plant air. The performance of an integrated unit can be derived from these tests on the basis of the specified compressor suction volume of 13,200 cfh. At design atmospheric conditions of 120 F ambient and 90 F, the mobile compressor of 13,200 cfh suction volume would deliver 11,200 standard (60 F, 30 in. Hg) cfh of dry air, and from Table 1 it can be seen that 1,000 scfh of 99.4% oxygen were produced at this air flow. This comes quite close to the design condition of 1,000 scfh of 99.5% oxygen at 120 F ambient, 90 F dew point. At more normal atmospheric conditions, such as have been used in testing the bulk of the units developed for the Services, the compressor delivery would rise to some 13,000 scfh of dry air from which, as shown in Figure 7, the M-7 unit produced 1,300 scfh of 99.45% oxygen (or 1,290 scfh of 99.5% oxygen). If the compressor could be speeded up to deliver 15,000 scfh, the cold box could deliver 1,500 scfh of 98.7% oxygen.

TABLE 1

Inlet temp. F	Air feed scfh	Production scfh O_2	Purity % O_2
135	10,000	840	99.7
135	10,500	1,000	99.2
135	11,000	1,000	99.4
135	11,300	1,000	99.2
135	12,000	1,000	99.7
138	14,000	1,180	99.6

It is of interest to note the large effect of extreme ambient conditions on production, namely, that though M-7 should be classified as a 1,000 scfh unit for extremely hot, humid climates, its classification would be 1,250 scfh for more usual atmospheric conditions. This difference in capacity is due to air delivery from the compressor, and is not due to the refrigeration cycle employed.

The M-7 unit was also run to make liquid oxygen. This was done by speeding up the expander to 300 to 350 rpm and allowing the liquid level to build up in the reboiler. When the level reached 12 to 13 in., liquid was drained off and weighed. The liquid produced in this manner was 17 lb per hr (equivalent to 200 scfh gas). In order to keep the purity from becoming too high some 500 scfh of gaseous oxygen were also withdrawn while liquid oxygen was being made.

Production Model of M-7 Unit

A flow sheet of the final production model (designated LP-1) is given in Figure 8. The LP units differed only slightly from the M-7. All the differences had to do with arrangement of equipment to conform to service desires and to allow maximum simplicity for production-line assembly.[13] Figure 9 is a picture of the trailer assembly which houses the complete oxygen plant. Figure 10 shows the plan

FIGURE 9. Clark mobile oxygen generating unit, Model LP-1.

view of the arrangement of equipment and Figure 11 shows several elevation group sections. The total weight of the LP-1 unit complete trailer mounted was 22,000 lb. Details of the equipment in this production model are summarized as follows.

Engine. Power for all moving equipment is supplied by a Lycoming 6-cylinder, air-cooled, modified aircraft engine through a rugged V-belt drive. The engine is flexibly coupled to a shaft bearing the main 9-in. diameter, 15-groove sheave. Both ends of the shaft are supported in self-aligning roller bearings. Normal operating speed is 2,400 rpm.

Dri-Air Compressor. The air compressor is a 6-cylinder, horizontally opposed, two-stage, air-cooled machine having six 5¼-in. bore and 3⅞-in. stroke, single-acting compressor cylinders (see Chapter 5). This machine is flexibly coupled to a shaft and sheave assembly supported at both ends by a self-aligning

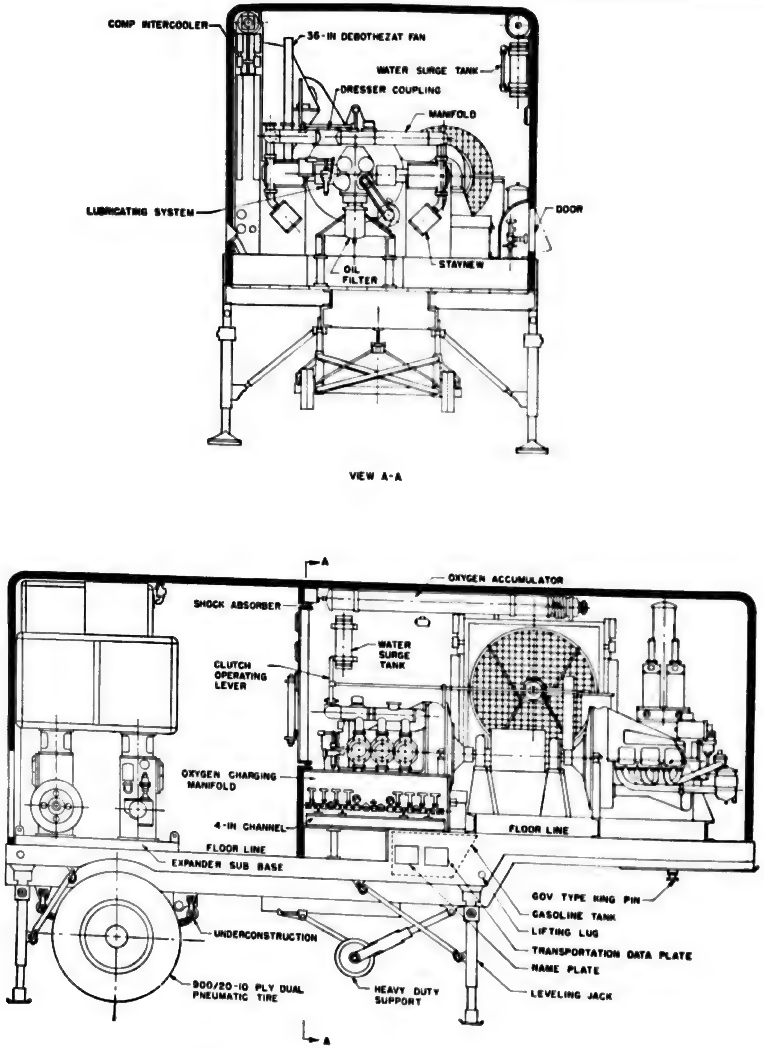


FIGURE 10. Elevation views of Clark LP-1 unit.

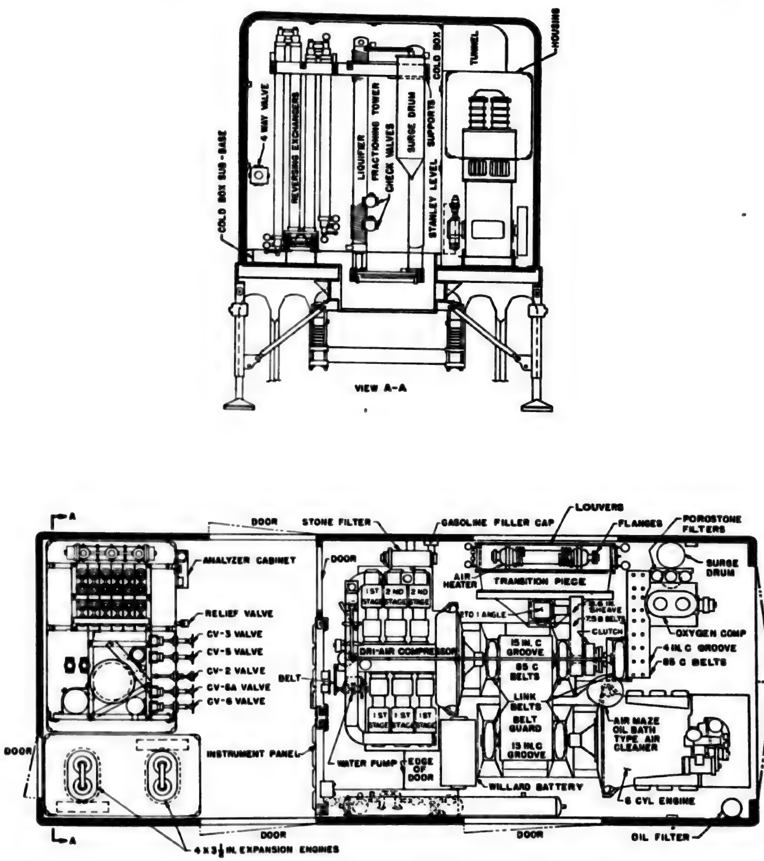


FIGURE 11. Clark LP-1 unit, elevation and plan views.

roller bearing. Power is supplied to this shaft by the engine drive shaft through 15 belts. The compressor, which operates at 1,600 rpm, is novel in that it utilizes Graphitar piston rings and packing rings, consequently requiring no lubricating and thus eliminating oil droplets from the air stream (see Chapter 5).

Coolers. The compressed air is cooled between stages directly against air in a radiator made of ⅜-in. OD Rome Turney finned tubes. Cooling air is supplied by an axial flow, 16-blade fan built into the road side of the trailer. The fan is driven by V belts from the air compressor shaft. The intercooler is designed

to cool all the compressed air and oxygen to a terminal temperature of 135 F when the ambient temperature is 120 F. The intercooler, besides having two air sections and four oxygen sections, carries a coil to provide cooling for the water circulating system. The water circulating pump takes its power from the air compressor auxiliary drive. Figure 12 is a picture showing the arrangement of the engine room on the trailer.

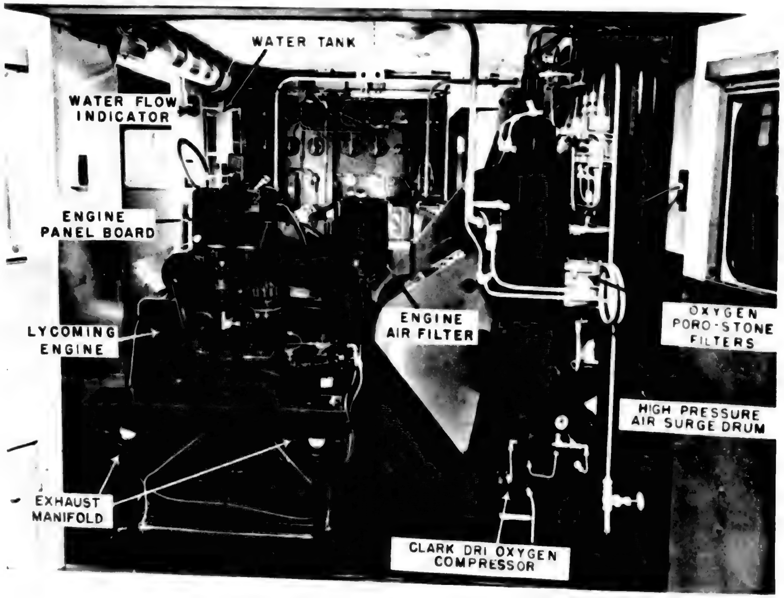


Figure 12. Engine room, Model trailer.

Heat Exchangers. The reversing exchanger consists of twenty-four 3 in. OD internally packed, Collins triple annulus exchanger tubes having effective packing lengths of from 5 ft 4 in. to 5 ft 3 in. (see Chapter 7). The tubes are arranged in six parallel rows of four tubes each, in series, so that an effective exchanger length of 19 ft 4 in. results. Air and waste nitrogen are alternately passed by two outer annuli, while oxygen flows continuously through the innermost annulus.

The liquefier consists of one 4 in. OD internally packed, Collins triple annulus exchanger tube having an effective packing length of 5 ft 5 in. The cold, low pressure nitrogen flows continuously through the three annuli while high pressure air flows through a series of spiral wound in. OD copper tubes wound around the outside of the 4 in. exchanger tube. Figure 13 is a picture of the cold box. The cold box is that part of the unit in which is placed all of the equipment handled at very low temperatures. The arrangements of heat exchangers and their manifolds is illustrated. Figure 14 is another picture of the cold box showing the heat exchangers on the right, the liquefier having a copper tube wrapped about it spirally, and the fractionating column at the front.

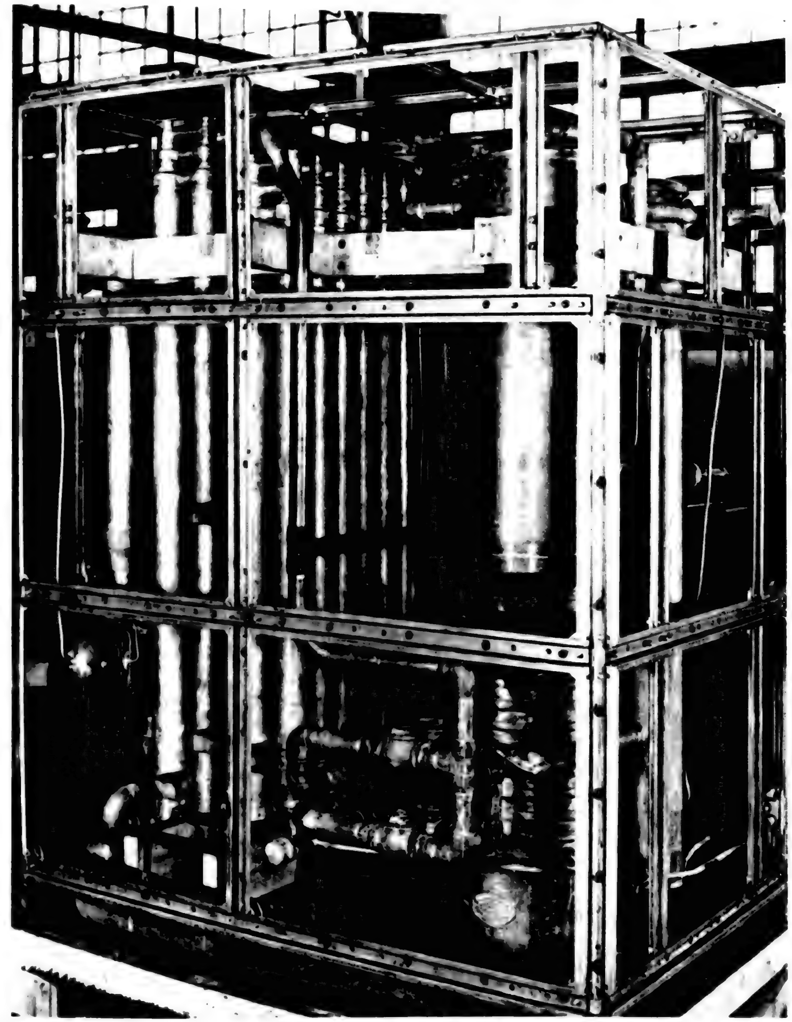


Figure 13. Assembly view Model LP-1 cold box.

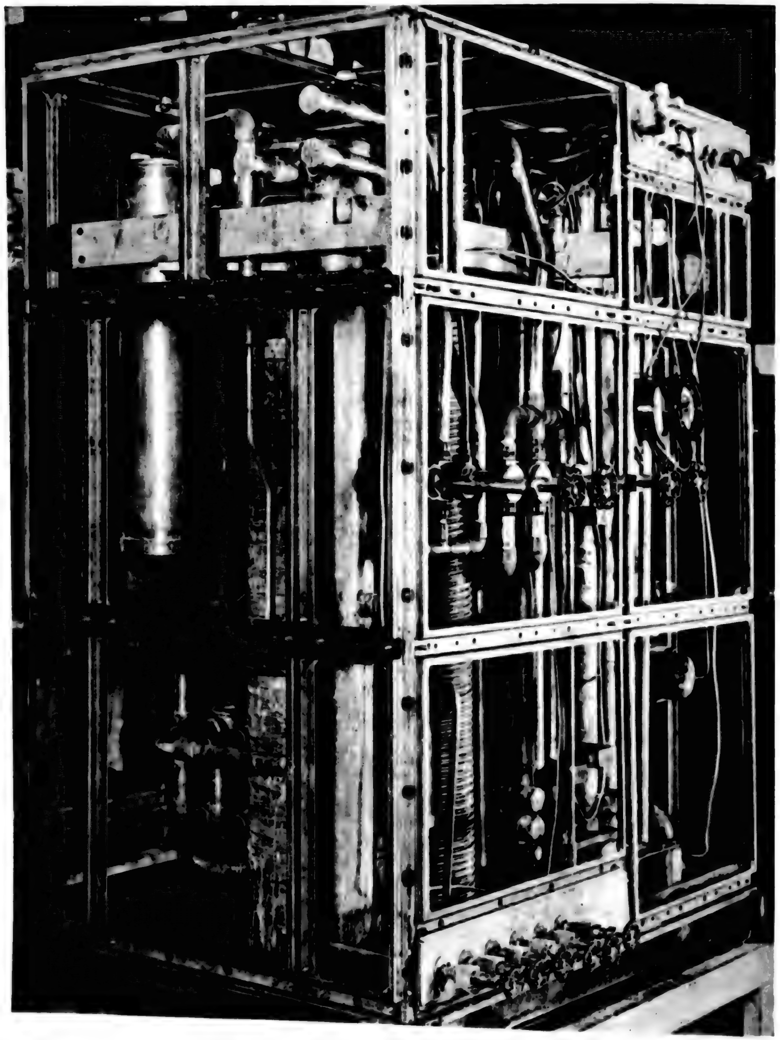


FIGURE 14. Assembly view Model LP-1 cold box.

Expansion Engines. The expansion engines are 2-cylinder, vertical machines having 4-in. bore and 3½-in. stroke (see Chapter 5). The expansion engine pistons are ringless, lap-fitted nitralloy operating in hardened nitralloy cylinders. These cylinders are surrounded by glass-wool insulation. Each crosshead of the machine is an integral compressor cylinder to absorb energy generated in the expansion end of the unit. Power is supplied for these machines by the expansion of the high-pressure air.

To provide ultimate safety in the operation of the dry oxygen compressor and to insure against losses in the expansion engine, circulating cooling water is employed to cool the oxygen compressor and the packing glands and heads of the expansion engine compressor.

All low-temperature piping is made up of Mueller Brass Company, or equivalent, solder fittings and copper tubing.

Fractionating Column. The fractionating column is a 29-tray rectangular bubble-cap, 12-in. diameter tower approximately 6 ft tall (see Chapter 8). Spacing between trays is 2 in. Vapor feed is provided for, five trays from the top. A glass cloth filtering medium removes any stray carbon dioxide ice from the tower reflux. Figures 13 and 14 show the column with heat exchanger equipment in the cold box. Further details and an operating manual for the production model are available.[13]

Dri-Oxygen Compressor. A 2-throw-crank, 4-cylinder, water-cooled, vertical, single-acting, tandem-type Dri-Oxygen compressor serves the cylinder charging end of the system (see Chapter 6). The machine will continuously charge five standard oxygen cylinders per hour to a terminal pressure of 2,200 psi. This machine utilizes Graphitar piston rings and consequently requires no water for lubrication. The compressor is driven through V belts by a Dodge clutch attached to the air compressor auxiliary drive shaft.

Oxygen Analyzer. A special design oxygen analyzer is provided. This is merely a modification of the standard ammonia type absorption analyzer unit.[14]

Instruments. Figure 13 shows the main instrument panel of the unit. The following types of instruments are supplied, all mounted on two large instrument panels facing the operating space in the trailer cab.

1. Pressure gauges used are the Crosby Steam Gauge & Valve Company, Style AAO and AIH, 4½-in. flush mounted, back connection gauges and supplied for the following points.

Service	Range, psi
First-stage discharge (air)	0 to 60
Second-stage discharge (air)	0 to 160
Expansion inlet	0 to 160
Tower top	0 to 30
Expansion engine brake	0 to 200
Oxygen first-stage suction	0 to 15
Oxygen first-stage discharge	0 to 100
Oxygen second-stage discharge	0 to 300
Oxygen third-stage discharge	0 to 800
Oxygen fourth-stage discharge	0 to 3,000

2. Temperature gauges used are (1) Tagliabue vapor-pressure thermometers[12,19] supplied for the following points:

Service	Temperature range, F
Cold high-pressure air	+200 to −315
Expansion engine discharge	+150 to −325
Cold low-pressure waste gas	+200 to −315

and (2) Weston Electrical Instrument Company Model 221D, 3-in. dial, 6-in. stem thermometers used at the following points. (These items are not mounted on the instrument board.)

Service	Temperature range, F
First-stage discharge (air)	50 to 500
Second-stage suction (air)	0 to 200
Second-stage discharge (air)	50 to 500
High-pressure air feed	0 to 200

3. A Meriam 16-in. Model A-275, panel-mounted, pot-type manometer is used for indicating liquid level in the low-pressure re-boiler.

4. A Mason-Neilan Type 414, size 1-in., 0 to 37 psi range reducing valve is used to control the suction pressure to the oxygen compressor.

5. A Bastian Blessing Company 8-cylinder, charging manifold arranged so that four cylinders at a time may be charged, is supplied complete with the necessary pigtails for connection to the oxygen cylinders. The pigtails have Linde right-hand connections, 0.903-in. diameter at the cylinder end. Oxygen cylinders are not supplied.

6. Time cycle controller made by the Taylor Instrument Company (No. 177-RJ-223 Flex-O-Timer) for operation on 110-volt, 60-cycle current is used to operate the 4-way air reversing valve.

7. A reversing valve, C. B. Hunt & Son, Model No. 9506-DP-4, 2-in. Quick-as-Wink double pilot

operated, 4-way valve, actuated by the Taylor Flex-O-Timer is used to switch the air from one side of the reversing exchanger system to the other in the LP-1 cycle. This valve is located in the cold box.

8. Miscellaneous instruments include the oil pressure and temperature gauges for the Clark Dri-Air compressor mounted on the instrument board, and the Weston Electrical Instrument Corporation tachometers for the expansion and Lycoming engines mounted on the instrument board.

The oxygen compressor and the expansion engines are each equipped with oil level and pressure gauges mounted directly on each individual machine.

3.2.3 Air Transportable Version of M-7 Unit

The M-7AT unit was designed and built to answer a need for an oxygen unit which could be transported by airplane and set up for operation at an advanced base.[22] The M-7 cycle was the basis of the plant and it was constructed with a view toward extreme compactness and lightness in weight. The plant was constructed in four sections, each of which was small enough to go through the doors of standard large military transport planes, and the weights of each section were within allowable air transportable limits. In the field the four sections can be connected rapidly by means of flexible hose and put into operation. Gasoline for fuel and power, and oil for lubrication were the only supply requirements aside from spare parts and tools. The units, completely boxed for shipping, had the following sizes and weights:

Skid	Dimensions (inches)	Weight for shipping (pounds)
Cold box	36 x 38 x 50	2,200
Air compressor skid	97 x 63 x 50	2,950
Oxygen compressor skid	81 x 48 x 66	1,950
Expander skid	27 x 50 x 65	1,175
Total weight		8,875

In addition to the above, there was required one box of spare parts and tools. Its size was approximately 30 x 30 x 60 in. and the weight about 300 lb.

The performance of the unit can be summarized as follows:

Cooling down period, 14 to 16 hr;
Flow of processed air, 12,000 scfh;
Operating pressure, 90 to 100 psi;
Expander speed, 300 rpm.

Production of the unit varies with purity and temperature of the surroundings. This can best be illustrated in the following table:

Inlet air			Oxygen drawoff	
Temp F	Dew point F	Pressure psi	scfh	Purity % O_2
46	45	90.5	674	99.51
103	40	92.4	586	99.57
120	80	94.6	536	99.48

Only one model of the M-7AT was built. It operated satisfactorily for a considerable period of time. It demonstrated the feasibility of constructing an extremely lightweight high-capacity unit for high-purity gas production. Fuel consumption amounted to 0.16 gallon of gasoline per lb of oxygen produced. The unit had the minimum of control valves and gauges. It required very little skill to operate the unit successfully. A complete description and performance data are covered in a series of reports.[16, 18, 20, 22]

Production Model.

When it had been demonstrated that the M-7AT would operate successfully, a procurement order was placed with the manufacturers of the LP (M-7) units for an air transportable model of the LP units.[13] Accordingly, a number were built using parts as nearly identical as possible to those previously described for the LP plant. Space rearrangements were made and there resulted a unit consisting of seven principle parts which could be conveniently connected and set up as shown in Figure 15. The general box construction of the units makes use of aluminum Lindsay structure just as was done for the M-7AT unit.

The following table gives weight data for each component part boxed for air transport.

Box	Dimension (inches)	Weight for shipping (pounds)
Engine	39¼ x 43¼ x 87¼	1,680
Air compressor	39¼ x 63¾ x 87¾	2,500
Oxygen compressor	72¼ x 55¾ x 52¾	3,010
Exchanger cold box	86¾ x 32¾ x 45¾	2,560
Tower cold box	98¾ x 34¾ x 39¾	1,860
Expansion engine	66¾ x 27¾ x 52¾	2,000
Total		15,110

Each box was of such size that it could be handled and loaded on a C-47 transport plane. The unit will

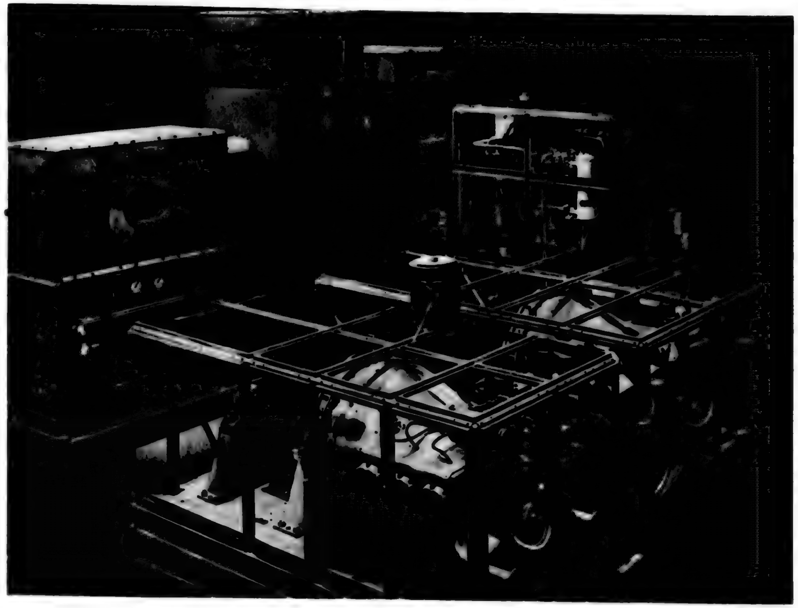


Figure 15. Clark air-transportable oxygen generating unit, Model LPAS-3.

produce 850 cfh of 99.5% oxygen with an ambient temperature of 80 F.

3.2.4 Medium-Capacity Air Transportable Unit—the M-3

At one time in the oxygen program it was thought that there might be a need for a unit to produce approximately 350 cu ft of high purity oxygen per hour. To meet this requirement an M-3 unit (cold box only) was built using the cycle found to be successful in the M-7 operation. The unit was to be a small lightweight one which could be transported by plane and set up at an advanced air base. Apart from the design of a smaller fractionating column than had been used on the AT unit, small Collins tubes were used and a new small reciprocating expander was developed. The M-3 was built and, after some trouble, operated successfully. No service demand developed for this size unit and the program was not carried beyond the point of demonstrating successful operation.

Design and operating data are thoroughly covered in OSRD reports.[11,22] The compact nature of the equipment can best be illustrated by Figure 16 which shows the cold box under construction.

3.3 LARGE-CAPACITY LIQUID OXYGEN PILOT PLANTS

3.3.1 Low-Pressure M-5 Unit

The Navy was interested in the development of a plant for the production of large quantities of liquid oxygen. A pilot plant, the M-5, was visualized and designed to produce 400 lb of liquid oxygen (95%) per hr from air at 100 psia, and to require no chemi-

cals for air clean-up or drying.[6] Other requirements were that the plant should be capable of operating on shipboard under the rocking conditions of a ship. It should operate for short continuous periods of 8 to 10 hr, after which it would stand idle for 14 to 16 hr, then operate again for another 8-hr period, and so on. These particular requirements for intermittent operation were later modified to make the operation continuous for a number of days at a time. The program on the M-5 was laid out with intermittent operation as the goal and the process design was made accordingly. A parallel development, the M-6, for the same goal but based upon 600 psi air pressure is described in the next section.

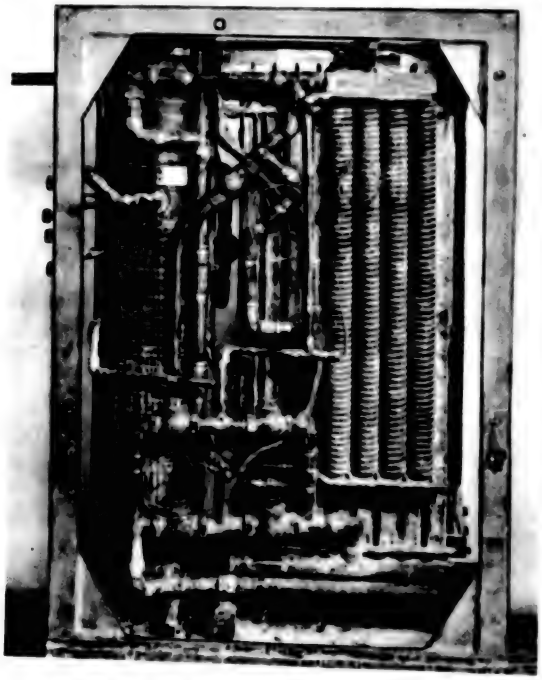


FIGURE 16. Rear view of M-3 cold box showing check valve assembly, liquefier, and exchangers.

When it was found that it would be more feasible to operate this large pilot plant on the M-7 cycle, the original M-5 process cycle was modified and the final M-5 plant is considerably different from that which was first visualized.[11,22] A maximum height requirement was specified at 14 ft. This requirement also had a definite bearing on the process layout. A single column-type cycle was required rather than a double column in order to meet the specifications.

THE KELLOGG M-5 REGENERATOR PLANT

A brief description of the original M-5 process follows.

Figure 17 is a flow sheet showing operating data for the original M-5 plant.[6,11] Design was based upon air having a maximum dry-bulb temperature of 100 F and saturated at 80 F. This air was cleaned of dust in a filter and compressed by a two-stage diesel-driven reciprocating air compressor to 100 psia. An intercooler and aftercooler were designed to cool the air to 95 F, with sea water entered at 85 F and discharged at 100 F.

Air from the aftercooler was passed through a centrifugal filter, a sintered metal filter and finally through a paper filter. These three filters removed all condensed water and oil particles from the air stream. Part of this cleaned air (about 75%) was used to supply the necessary refrigeration and the remainder was liquefied and fractionated. The clean air passed warm and switching valves and went to regenerators where it was cooled to −230 F. All water and carbon dioxide were frozen out in the regenerators. Four regenerators were used, arranged in two pairs. The high-pressure air was switched from one to the other of each pair at 3-min intervals. The switching of the two pairs was staggered. The reversing valves mentioned previously were controlled by an interval timer which utilized a pneumatic device for activating the valves. Check valves were provided at the low temperature and the regenerators. By this arrangement, air passed through two regenerators in parallel giving up heat to the packing which had been cooled previously by the effluent waste gas. Impurities in the air (CO_2, H_2O, hydrocarbons, etc.) were deposited in the regenerator packing but were not completely removed by sublimation and evaporation by the returned gas in the reverse period of the cycle.

The cold air leaving the regenerators passed through a bed of silica gel for the purpose of equalizing variations in temperatures of the cold gas, to remove most of the hydrocarbons and solids not removed in the regenerators, and to provide additional volume to reduce pressure surges which occur when the regenerators were switched. During the start-up operation of the plant, the silica gel was used to remove the last traces of water from the air to prevent freezing in the passages leading to the expander.

After the equalizer, the main air stream was divided so that about 25% passed to the liquefier and about 75% was sent to the turbo-expander. The

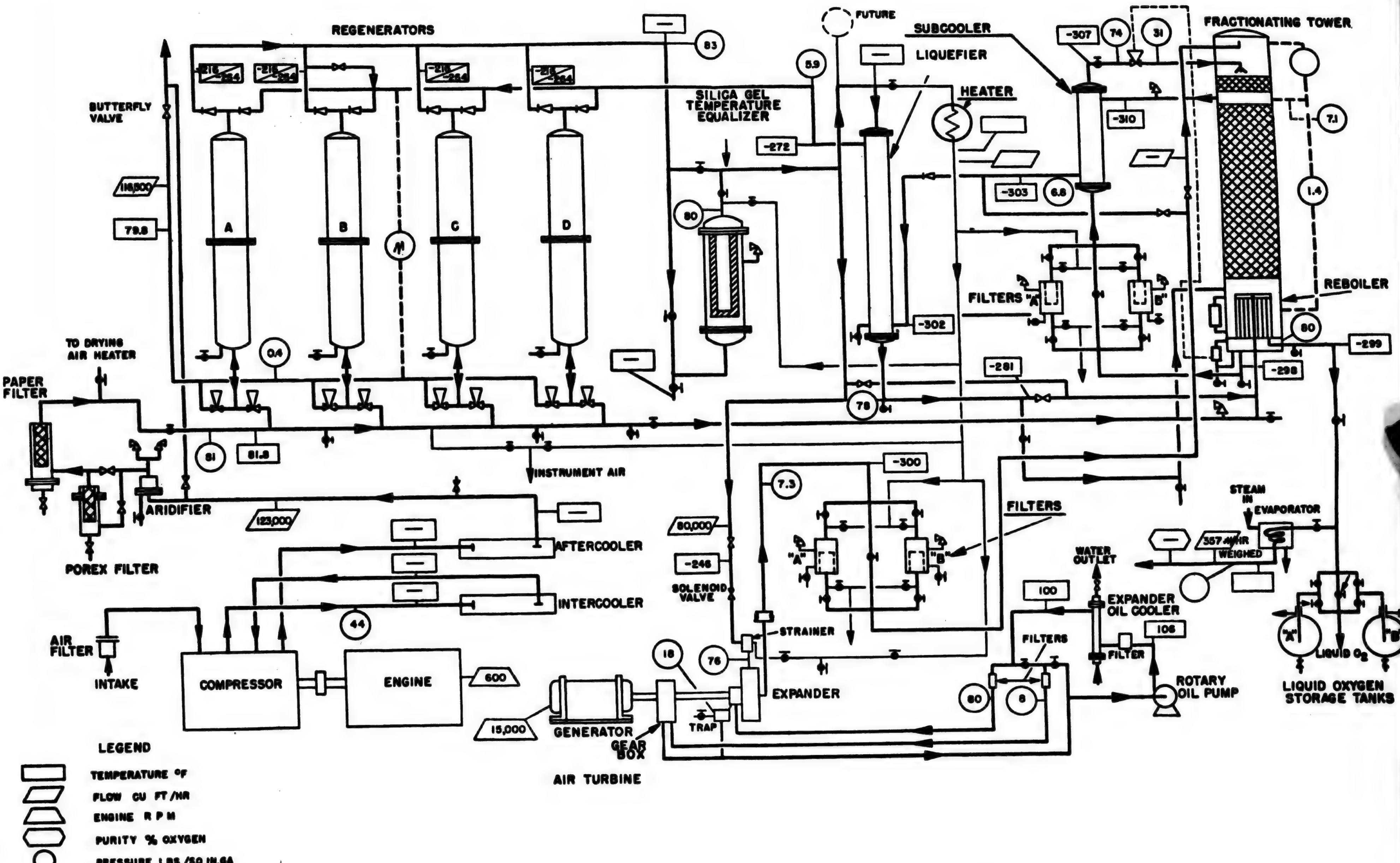


FIGURE 17. M. W. Kellogg Co. pilot liquid oxygen unit M-5, 400 lb/hr, mechanical low-pressure system, process flag sheet.

liquefier served as a partial condenser for the air to be processed. The air passing through the turbo-expander dropped in temperature from —230 F to —308 F. This temperature drop was accompanied by a pressure drop from about 90 to about 22 psia. The energy given to the expander during the expansion of the gas was absorbed through a set of gears by an electric generator. In the pilot plant the current from the generator was absorbed by a bank of resisters. A cloth filter was provided beyond the expander outlet to filter out any solid carbon dioxide which might have been precipitated during the expansion. Part of the expanded air was introduced into the fractionating column very near the top and acted as a vapor feed. The remainder of the expanded air was sent to the liquefier and then, together with effluent from the tower, was sent to the regenerators.

That part of the air stream which passed through the liquefier was sent to the tubular reboiler at the bottom of the fractionating tower where it was completely liquefied. This condensation took place at about —284 F under a pressure of 80 psia. The condensing of this air stream provided the heat to reboil the liquid in the bottom of the fractionating tower. The liquid air from the high-pressure side of the reboiler passed through a filter to remove any solid carbon dioxide particles, passed through a subcooler countercurrent to tower overhead and was cooled to —297 F. Having left the subcooler it passed through an expansion valve and provided the liquid reflux as well as rich feed for fractionation. Liquid oxygen on the low-pressure side of the reboiler was withdrawn as product.

Waste gas, rich in nitrogen, was taken from the top of the tower through the subcooler and liquefier and back to the regenerators. Figure 18 shows the diesel and compressor for the M-5 unit and Figures 19, 20, and 21 are pictures of the cold box. Operating characteristics of the M-5 regenerator plant are given in Table 3.[11] The operating record of the M-5 plant with the regenerators is shown in Table 2.[15,17]

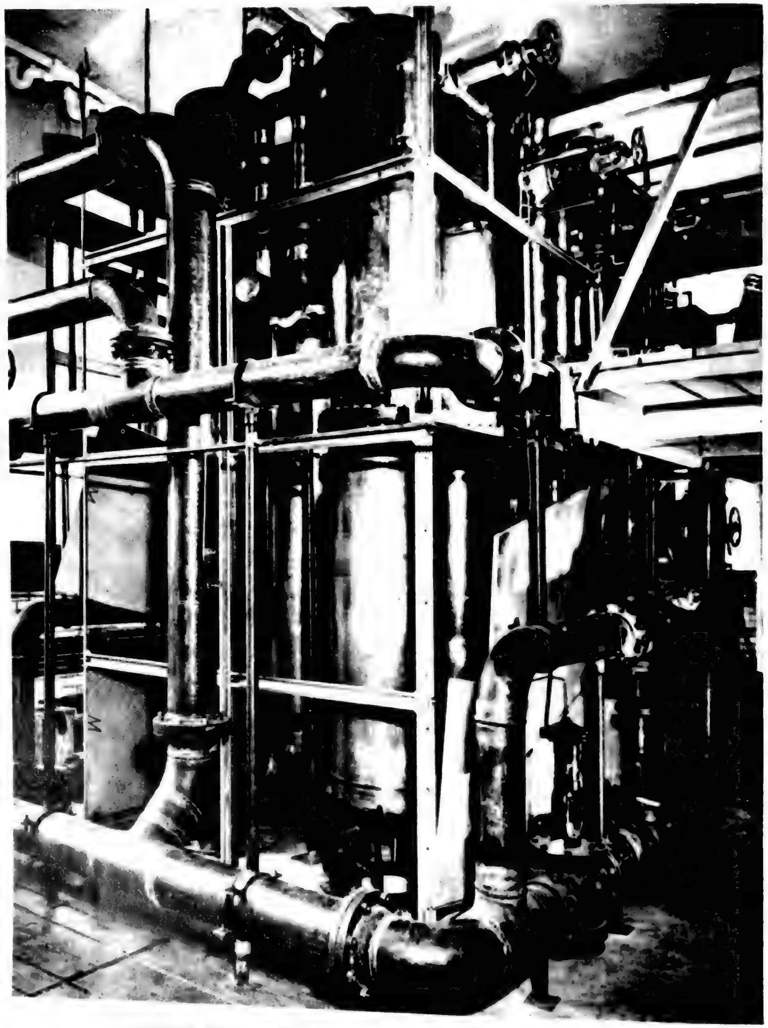
There were two principal difficulties in the operation of the M-5 unit in its original form with regenerators. The Stedman fractionating tower proved to be inadequate and difficult to operate (see later chapter on fractionation). The poor tower performance resulted in low-purity oxygen although such production did not interfere with the rate of liquid production or result in serious changes of condition in other parts of the plant. It was found that regenerator plugging was quite rapid and thawing or shutdown was necessary at intervals of from 6 to 12 hr. Various thawing methods were tried, but none of them permitted uninterrupted operation of the plant for long periods of time. The plant, however, did meet original requirements regarding intermittent operation but by the time the M-5 plant was operating, the

FIGURE 18. Diesel engine and compressor—inter-coolers at right, M-5 unit.

M-7 cycle had been proven satisfactory. It was therefore felt desirable to incorporate the reversing heat exchanger principle in the M-5 plant and after the runs listed in Table 3, the plant was revamped to install Collins heat exchangers.[22] One very notable achievement had been marked during these first runs of the M-5 plant, namely, the very successful operation of the turbo-expander. This work is covered in detail in Chapter 5. Complete specifications, process calculations and experimental results for the M-5 plant are found in other reports.[11-22]

THE M-5 HEAT EXCHANGER PLANT

The M-5 cycle was revised primarily to change from the use of regenerators to the reversing heat exchangers. In addition a tray column was designed especially for the unit (see Chapter 8) and a number of minor changes made as a result of previous operating experience. For the most part, these later changes simplified the equipment and operation. The



[illegible]

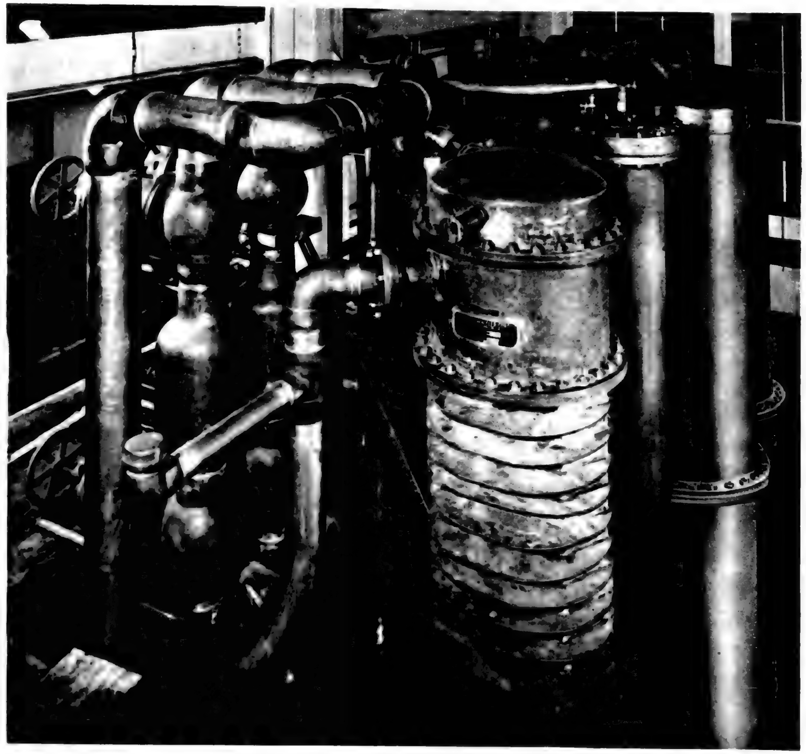


FIGURE 20. Uninsulated cold box—end view showing tower and G-3 low-pressure filters, M-5 unit.

four regenerators were replaced by two parallel banks of Collins type heat exchangers. Thirty exchanger tubes were used in each bank. Their location in the unit is shown in Figure 22. Figure 23 shows the M-5 plant ready for operation with the control board on the left and the turbo-expander installation at the right. The revised flow sheet is shown in Figure 24, together with operating data showing production-rate and operating characteristics.

The M-5 plant with reversing heat exchangers differs in several particulars from the M-7 flow sheet of Figure 5. In the first place, the M-5 cycle is designed for liquid oxygen production, whereas the M-7 cycle is designed for gaseous oxygen production. The M-5 requires much more refrigeration per lb of oxygen produced than does the M-7 plant, simply because one plant produces liquid, whereas the other produces gas. The other principal difference between the two cycles is that the "unbalancing" stream in the M-7 cycle makes use of low-pressure nitrogen whereas the unbalancing stream in the M-5 plant makes use of high-pressure air. It has been shown

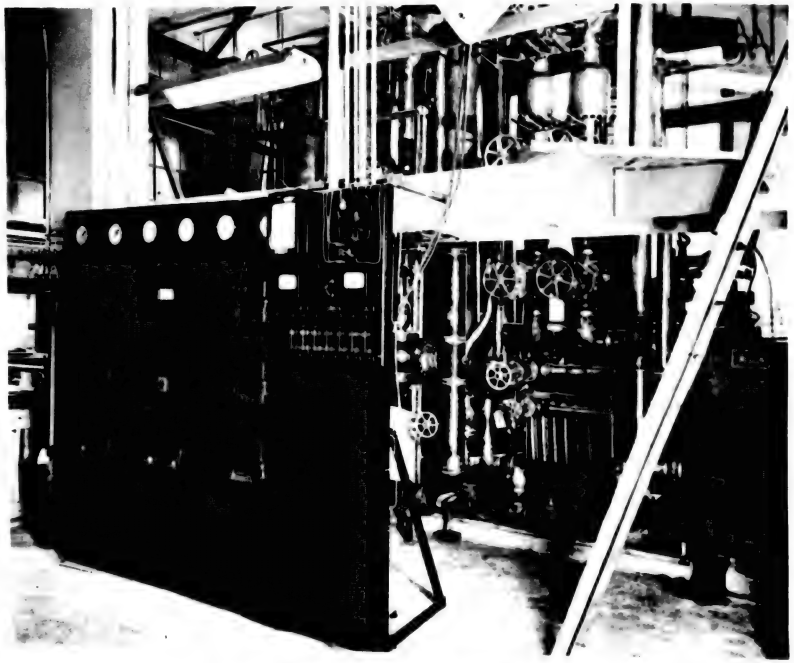


FIGURE 21. General view of insulated cold box, M-5 unit

that carbon dioxide removal is completely achieved more easily by the high-pressure air unbalance rather than low-pressure unbalance.

The performance of the exchangers was in general much superior to that of the regenerators. It was possible to operate continuously for long periods of time (upwards of 10 days). Some further experimentation is still necessary, at this writing, to arrange the heat exchanger system and the filtering mechanism between the aftercooler of the compressor and the cold box to insure complete removal of entrained water from the compressor air. Performance data on the operation of the plant is covered in detail elsewhere.

A further development in the design of reversing exchangers has led to a much more compact and efficient reversing heat exchanger than the Collins design. This rectangular heat exchanger described in Chapter 7 is being constructed in a large size, suitable for installation in the M-5 unit. These heat exchangers are to be installed and, after other minor modifications, the plant will be ready for further tests. It is anticipated that continuous performance over long periods of time can be achieved by the new heat exchanger and process arrangements.

3.3.2 Intermediate Pressure Air Reduction Company M-6 Unit

Paralleling the low-pressure liquid oxygen pilot plant M-5, a medium pressure cycle was devised and a plant constructed for the production of approximately 100 lb per hr of liquid oxygen with a purity of at least 95%. The air pressure used in the plant

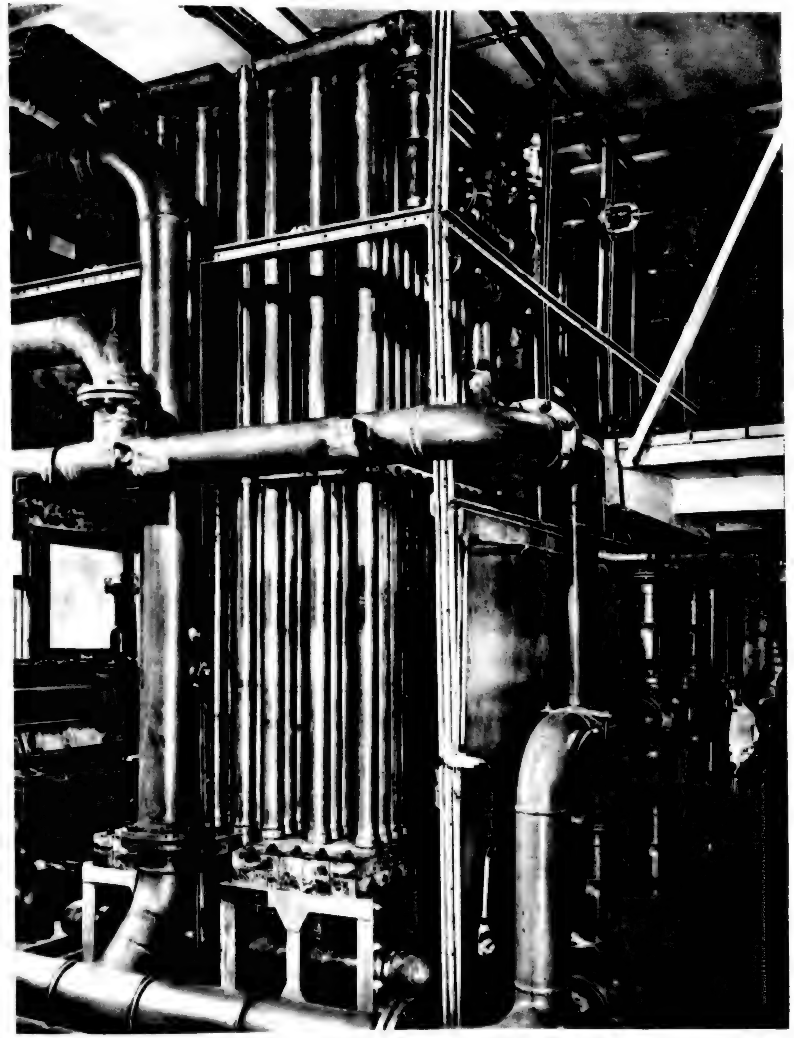


FIGURE 22. Cold box of M-5 unit showing reversing heat exchangers and air piping.

Table 2. M-5 operating record.

Run No.	Starting date	Actual operating hours	Cause of shutdown	Subsequent revisions
1	5/19/44	28	Compressor coupling failure	Revised tower distributor; revised equalizer flow.
2	6/ 5/44	156	Voluntary	Revised tower distributor and turbine nozzles; installed equalizer dust filter and regenerator control dampers
3	8/ 1/44	14	Turbine bearing failure	
4	8/10/44	44	Liquefier and generator failure	
5	9/12/44	12	Expander oil pump failure	
6	9/19/44	115	Numerous	Enlarged regenerator dampers; installed tower feed meter.
7	10/19/44	160	Voluntary	Revised tower distributor, reflux filters, and turbine nozzles.
8	12/ 8/44	110	Voluntary	
9	2/13/45	10	Voluntary	Substituted reversing exchangers for regenerators and Type J tray tower for Stedman tower. Removed turbine exhaust filters.
10	5/ 9/45	170	Exchanger plugging probably with CO_2	
11	5/30/45	240	Voluntary	

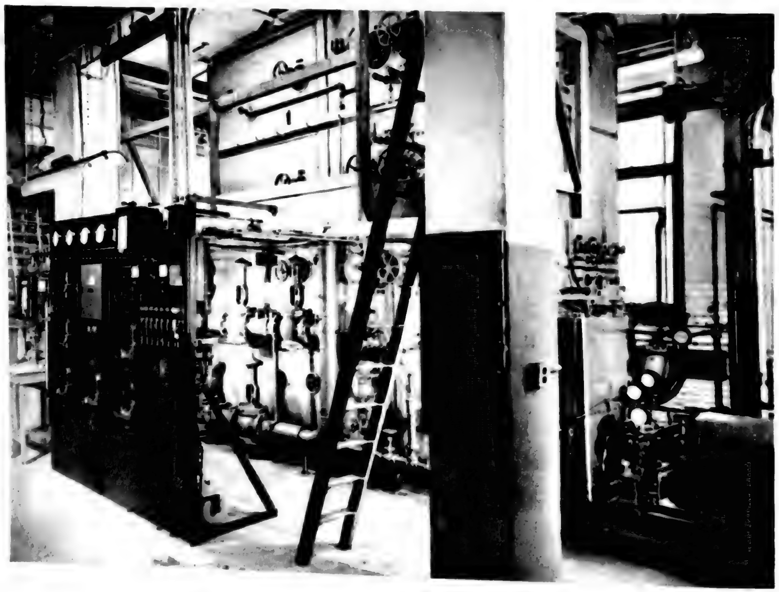


Figure 23. M-5 unit—cold box installation and panel board.

Table 3A

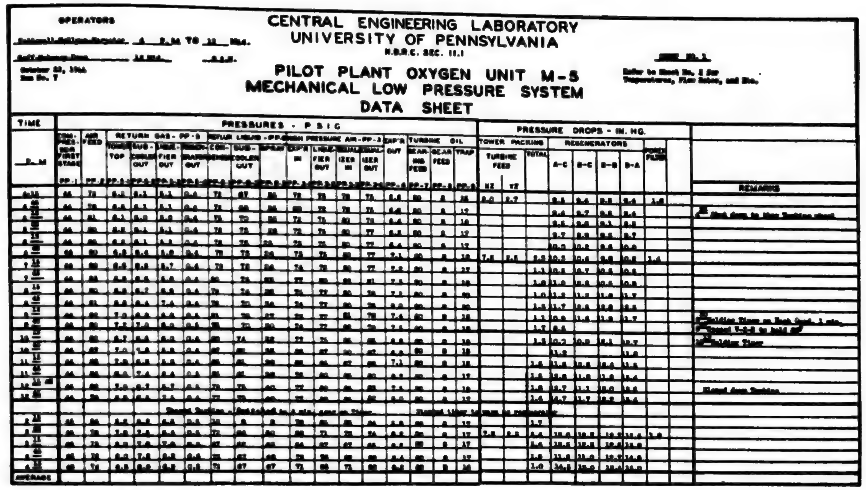


Table 3B

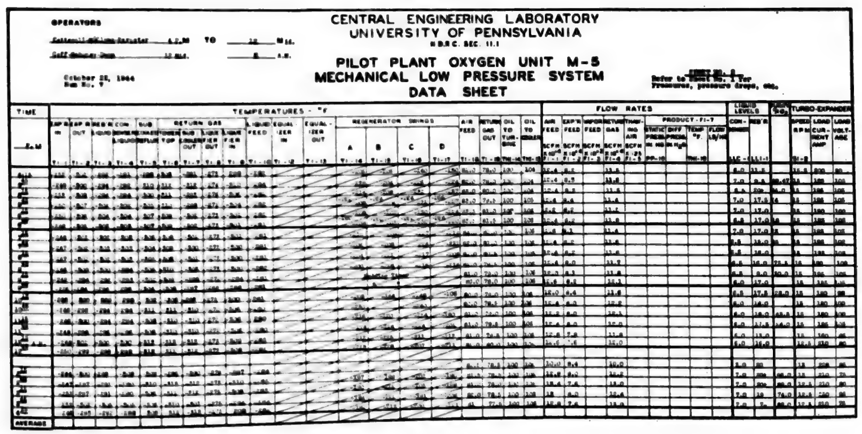


TABLE 4

PILOT LIQUID OXYGEN UNIT M-6
MECHANICAL MEDIUM PRESSURE SYSTEM
DATA SHEET

P.M. TIME	PRESSURES, P.S.I.G. — H.P. AIR	PRESSURES, P.S.I.G. — MEDIUM PRESSURE AIR	PRESSURES, P.S.I.G. — RETURN GAS	TEMPERATURES °F — H.P. AIR	TEMPERATURES °F — EXPANDERS	TEMPERATURES °F — MED. PRESSURE AIR	TEMPERATURES °F — RETURN GAS	FLOW RATES LBS. PER HR.	PRODUCT	LIQ. LEVEL	H.P. EXP. (...)
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

was 600 psia. The low-pressure M-5 plant of maximum compactness was ultimately dependent for successful operation upon the development of an efficient high-speed rotary air compressor and on the successful development of an efficient turbo-expander. Further, it was necessary to develop mechanical means for elimination of carbon dioxide, water, etc., from the low pressure air stream. At the beginning of the program equipment was not available for achieving such a plant, although there was considerable promise of success. In contrast to the low-pressure M-5 cycle, a medium-pressure process operating at about 600 psia could make use of reciprocating compressors of standard design or lightweight compressors which might be developed for this particular pressure. Reciprocating expanders were already available to supply refrigeration for such a unit although it was felt desirable to improve the design of commercial expanders available at that time. For carbon dioxide and water removal, switching heat exchangers and cloth filters were thought to offer excellent possibilities for success. Owing to the higher pressure of operation, many of the heat exchanger elements and piping could be reduced in size more than that required for the lower pressure unit. It was felt that carbon dioxide and water could be removed successfully by mechanical separation, filtration, and switching. The two cycles, M-5 and M-6, thus represented two distinctly different processes whereby air could be compressed, cleaned and used for all necessary refrigeration. The two processes were developed at the same time with the hope that at least one of them would prove successful in all respects. The lower pressure cycle seemed to offer greater possibilities for simplified lightweight very large capacity plants with high efficiency, whereas the M-6 cycle offered the best possibility for quickest realization of the immediate Navy requirements for large liquid oxygen plants.

The general specifications for the M-5 and M-6 pilot plant follow.

Production over 400 lb per hr of liquid oxygen at 95% purity or better; power consumption to be 0.5 brake horsepower per lb of liquid oxygen.

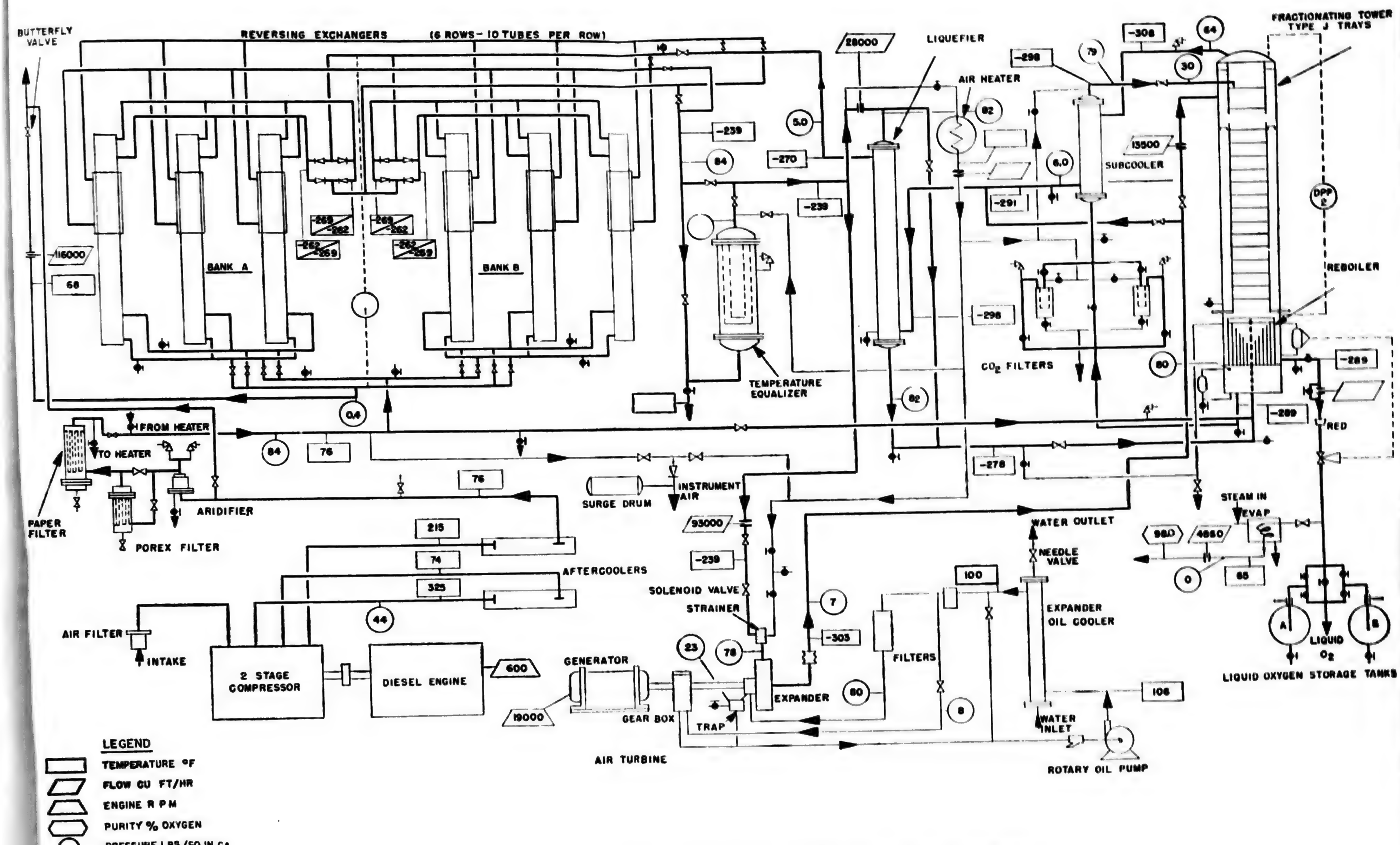


FIGURE 24. M. W. Kellogg Co. pilot liquid oxygen unit M-5, 400 lb/hr, mechanical low pressure system, process flagsheet.

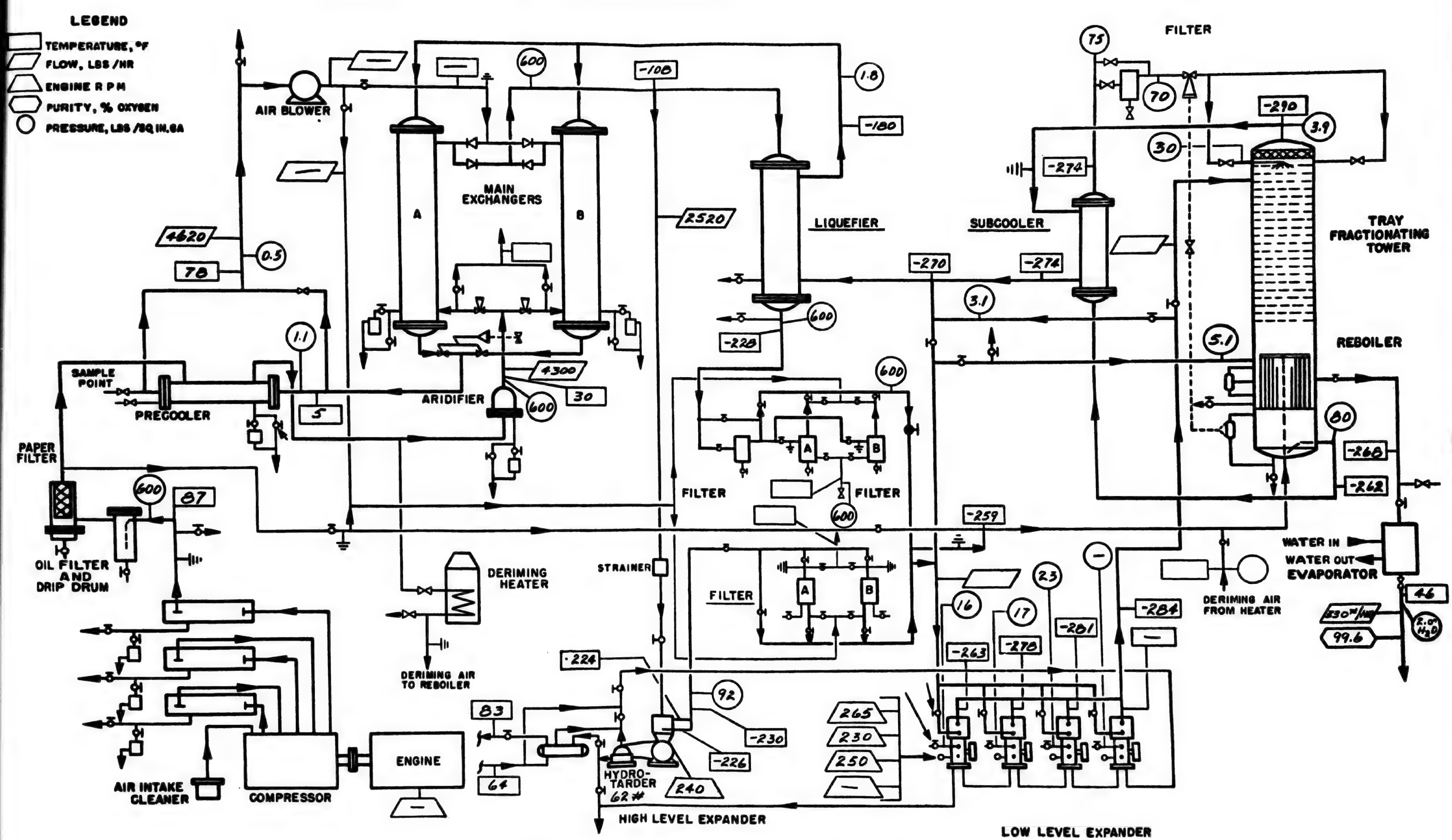


FIGURE 25. M. W. Kellogg Co. pilot liquid oxygen unit M-6, process flapsheet.

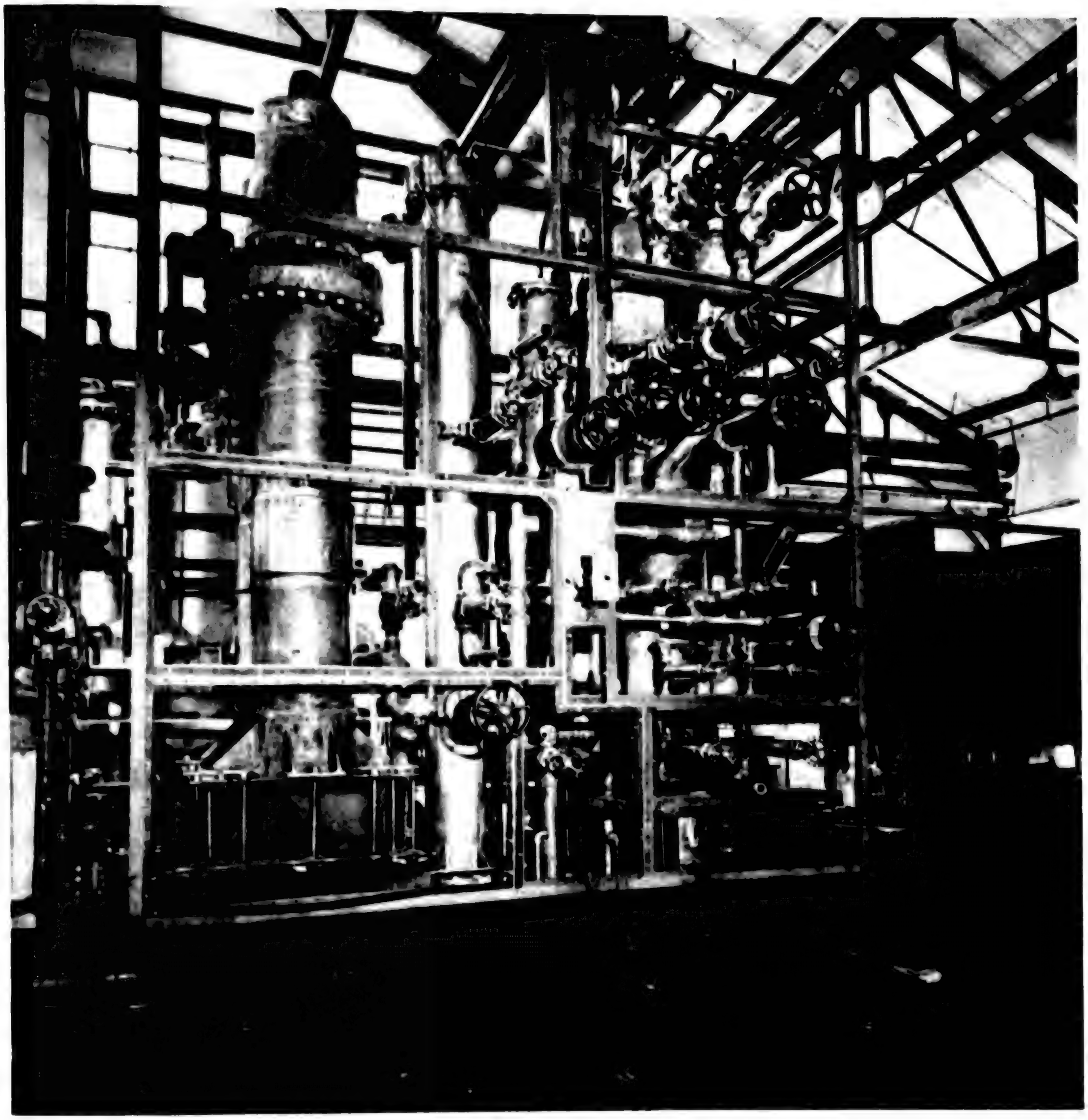


FIGURE 26. Front view M-6 unit.

The plant to operate under rocking conditions of 6 cycles per min at 15 degrees from the vertical in any direction.

Total space to be occupied by the plant, including air compressor, to be 15 x 17 x 15 ft high. This severe space limitation practically ruled out the use of chemicals and water and carbon dioxide removal and in any event it was highly desirable to develop a plant which would not require chemical supplies for such purposes.[23,24]

The designed process flow sheet for the M-6 plant is shown in Figure 25.

The process was designed to operate as follows:

Air at 100 F saturated at 80 F is drawn through a dust filter to a three-stage diesel-driven reciprocating compressor and discharged at 600 psia.

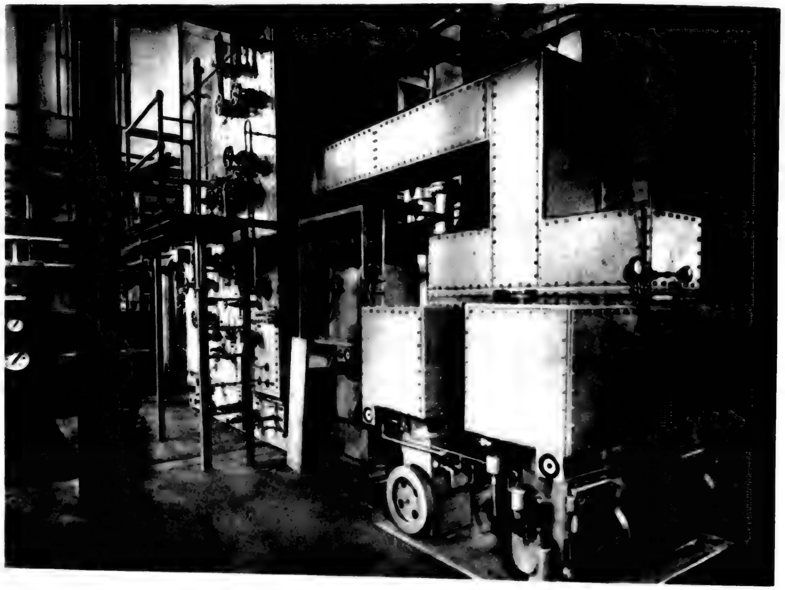


FIGURE 27. M-6 pilot plant [illegible]

Two inter-stage coolers and an aftercooler reduce the temperature of the air to 95 F with sea water at a maximum of 85 F at the inlet and 100 F at the outlet. Air from the aftercooler is passed to a drum in which condensate is cooled and removed. The air then passes to an oil filter where paper or glass and oil particles are separated from the air.

All refrigeration required in the process is obtained by the use of expansion engines operating at two different pressure levels. [illegible] part of the air entering the system is used for refrigeration and the remainder is liquefied and separated to obtain the liquid oxygen product.

The dirt free, high-pressure air is cooled to about 40 F in a precooler, located [illegible] where the bulk of the water vapor is condensed and removed as liquid through a [illegible] then passes to one of two [illegible] so that while [illegible] Air is cooled [illegible]

to about 130 F and any water vapor which remains after the precooler is frozen out and allowed to accumulate in the shell of the exchanger. After a suitable period of time, and before the exchanger is fouled badly by accumulated ice, the parallel exchanger is switched into the stream and a blast of warm dry effluent gas from the process is allowed to pass through the exchanger with accumulated ice. This process is repeated cycle wise throughout the operation. The cold air from these exchangers is passed to a liquefier where it is cooled below the critical temperature, and a portion of it is liquefied. This mixture of cold and liquid air then proceeds to the high-pressure side of the reboiler where it is completely liquefied and gives up heat to the boiling oxygen in the column. The liquid air then passes through a subcooler, a filter, and a reducing valve from which it passes directly to the top of the tower supplying [illegible] reflux. The other portion of the air from the main exchanger is taken to a high level expansion

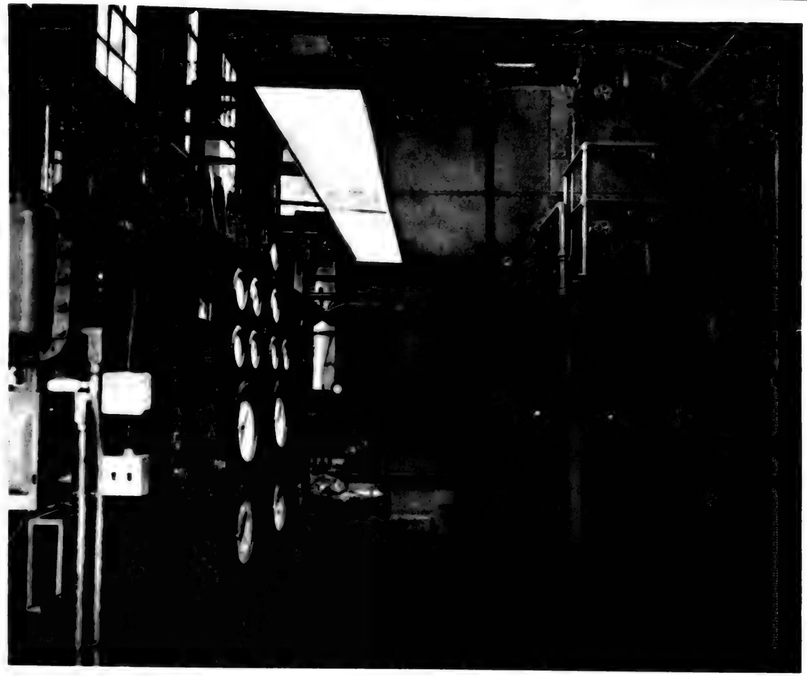


FIGURE 28. M-6 pilot plant—operating space—instrument panel and controls.

engine where pressure is allowed to drop to 74 psia. The corresponding temperature drop is from −130 F to −250 F. Solid carbon dioxide is precipitated during this temperature change and a cloth type filter is used to block the flow of the solid carbon dioxide. The filters are a parallel pair and can be used alternately so that from time to time they can be blown free of solids. Part of the filtered 74 psia air stream is taken to a set of four low-level expansion engines, where the air is expanded to about 16 psia and its temperature is reduced to about −285 F. The 600 psi filtered air from the liquefier is expanded to 74 psia and is then mixed with the remainder of the 74 psia stream and subsequently filtered in cloth-type filters.

The air exhaust from the low level expanders is fed into the fractionating column near the top and acts as a vapor feed. A small amount of oxygen is recovered from this stream. Liquid oxygen is withdrawn from the bottom of the column, and vapors, rich in nitrogen, are taken from the top of the column and their refrigeration recovered by passing through the subcooler, the liquefier, and the main exchanger to the precooler. The equipment was designed to allow discharge of the effluent gas at 7 F below the temperature of the high-pressure feed.

Details of individual pieces of equipment and their operating characteristics are given in later chapters; for complete reference see OSRD reports.[11,22] Figures 26, 27, 28 are views of the pilot plant. Table 4 is a typical operating data sheet for the M-6 plant.

Plant operation was achieved for extended periods

of time and after proper operating technique was developed, it was found that carbon dioxide and water could be removed by the switching exchangers and filters. It should be remembered that original specifications for these large liquid oxygen plants require them to operate for short periods of time only. The M-6 plant has been demonstrated to be capable of operating for production periods of 8 to 10 hr, followed by 10- to 20-hr periods of shutdown. In this intermittent type of operation no difficulty is experienced with water or carbon dioxide blocking and the unit achieved its original goal. The test runs showed, however, that it was also possible to operate for longer continuous periods. This now seems to be the desirable method of operation, and the unit is satisfactory for such purposes. The best performance for an extended period of time gave the following results:

For a continuous 72-hr period with head pressure 600 psi and air flow 4,100 lb per hr, there were produced 418 lb per hr of liquid at net horsepower requirement of 323, corresponding to 0.77 hp per hr per lb of liquid oxygen; the oxygen purity was 99.5% and oxygen recovery was 44%.[24]

Chapter 4

HIGH-PRESSURE CYCLES AND UNITS

By *J. H. Rushton*

4.1

INTRODUCTION

For certain requirements of the services it seemed advisable to develop oxygen production plants based upon high pressure cycles. Six separate projects were carried through to completion, based on high-pressure air for production of both gaseous and liquid oxygen. Two of these units were developed primarily for use aboard a submarine, where extreme compactness in size was desired, and where the unit was designed to produce liquid oxygen for storage for breathing purposes aboard the submarine. The other four units were built for mounting on a trailer or on shipboard, using torpedo-charging compressors to supply this high-pressure air. In addition it should be noted that a so called intermediate pressure (600 psi) plant (M-6) is described in Chapter 3.

4.2

KEYES UNIT

A direct expansion refrigeration plant of very compact design has been perfected, and several models built, leading to a design suitable for mass production.[3-6,10] The original desire for a compact plant to produce liquid oxygen for replenishing the gaseous oxygen of a submarine atmosphere resulted in the first of the Keyes units. The unit was to be supplied with air from compressors normally used to charge high pressure air into the submarine torpedo charging flasks. These submarine torpedo charging compressors had a normal capacity of 300 lb per hr of air discharged at 3,000 psi. The unit was to be of such dimensions as to pass through the conning tower hatch of a submarine. With the available air supply, the unit was designed to produce from 15 to 18 lb per hr of 98+% liquid oxygen when operated without any precooler refrigeration. With the aid of a Freon refrigeration machine to effect forecooling, production was anticipated at between 35 to 40 lb per hr. A prototype was built and operated successfully; a flow sheet for it is given in Figure 1.[2] The cycle is a simple high-pressure Joule-Thomson one with water and carbon dioxide removed by alumina and solid caustic soda. The alumina is contained in cylinders and can be re-activated; the caustic is in pellet form in cylinders and can be replaced from time to time. Warm, dry, CO_2-free, high-pressure air is led to the unit where it enters heat exchangers which may or may not be attached to a Freon forecooling machine. The clean high-pressure air is cooled by countercurrent heat exchange with nitrogen effluent and passes through the condenser side of the reboiler. It then passes through an activated carbon filter for the removal of the last traces of carbon dioxide after which it passes through an expansion valve where the pressure is released from 200 atmospheres to approximately 1 atmosphere. Feed and reflux are supplied from this stream and boiling liquid oxygen is removed from the reboiler as production. Effluent nitrogen from the top of the column is returned through the heat exchangers and is used for re-activation of the alumina.

Four manufacturing models of the Keyes unit were made and equipped for use with or without Freon forecooling.[4] Two of these models were sent to Great Britain for tests and two were retained for use in NDRC and Navy laboratories. The cold box was constructed within an aluminum cylinder 18 in. in diameter and 15 in. in height. This contained all the heat exchanger and rectifying equipment. The total weight of this part of the unit was 175 lb. The oil-water separator, caustic soda tube, and aluminum drying tubes were contained in cylinders 48 in. long and of various diameters up to 6 in. The total weight of this cleanup equipment was about 450 lb. It was mounted on a single frame adjacent to the cold box. An air-cooled Freon refrigeration unit, weighing 470 lb complete with motor, occupied a space of 39 x 31½ x 25 in. high. A flexible delivery tube was provided for conveying the liquid oxygen production from the unit to suitable storage flasks. Another feature of this high-pressure plant is its short start-up time. Liquid oxygen can be drawn off the unit within 45 to 60 min after operations are started. These are the conditions when the unit is completely warm. After the unit is cool, a shorter time of start-up can be obtained. Figures 2, 3, and 4 are pictures of the Keyes unit. These units have operated very successfully and have proved to be rugged and thor-

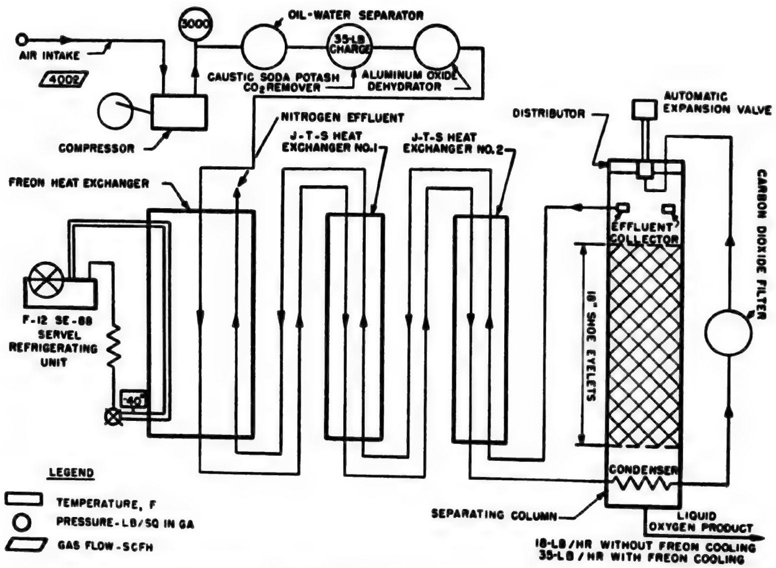


FIGURE 1. Keyes submarine air conditioning liquid oxygen unit.

oughly dependable. Several of the automatic features, particularly the liquid level control and the automatic expansion valve, have proved to be most satisfactory. One of these units has been in almost daily use for several years supplying liquid oxygen for experimental purposes in the Central Engineering Laboratory of this Section. It operates without difficulty and requires the minimum of attention and maintenance.

By the time the four models just mentioned were produced, there was under development an air-activated liquid oxygen pump (see Chapter 6). Furthermore, it was felt desirable to extend the usefulness of the Keyes unit from a liquid producer to a gaseous oxygen producer. The liquid pump, applied to the Keyes unit, would enable it to produce gaseous oxygen at high pressure [illegible] so desired. With these advantages in mind, a [illegible] Keyes unit was laid out and a prototype [illegible] pump unit was built, incorporating the liquid [illegible] in the Keyes unit. This pump model was successful in operation and a design was laid out for production models of the Keyes unit with liquid pump. It was also desirable to produce higher purity oxygen (99.5%) for engineering and aircraft breathing purposes. It was decided to incorporate a rotating column in the unit to allow operation under rolling conditions as encountered on surface ships of the Navy, and to step up the capacity of the unit so that 540 lb per hr of air at 3,000 psi (120 cfm) could be used. On this basis, oxygen production should be at least 70 lb per hr. Forecooling by Freon was provided when liquid oxygen was to be the product, but was not required for the production of gaseous oxygen at 2,000 psi. Further, for production of high-pressure gas, the air feed pressure could be reduced. A flow sheet of the pump unit is given in Figure 5. Two such pump units are now in the course of construction. They will be rectangular and will occupy a space approximately 3 x 5 x 7 ft high, without air compressor.[3,10]

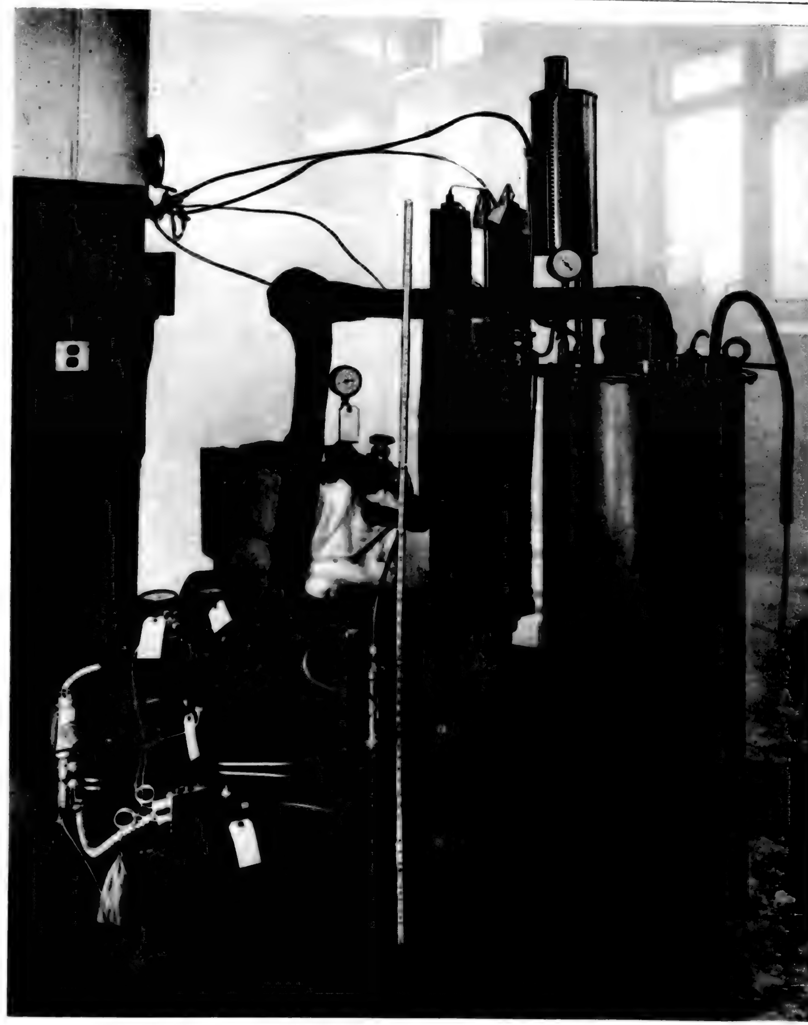


FIGURE 2. Keyes S-1,000 unit (335 lb) connected to Freon forecooler (1,000 lb) and showing cleanup system (900 lb) in center background. Liquid O_2, 35 lb per hr, 98+ per cent purity.

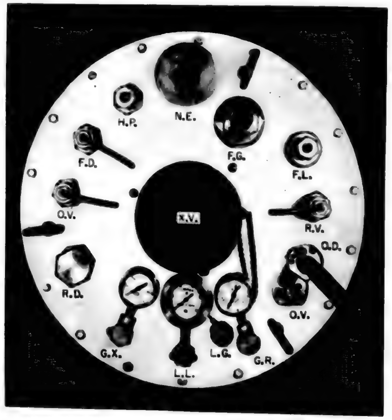


FIGURE 3. Keyes unit, Servel model. Top plate assembly.

H.P. High pressure air connection
N.E. "Nitrogen" effluent outlet
O.D. Oxygen product (liquefied) delivery
Liquid level attachment joints:
L.L. Liquid at bottom of rectifier
L.G. Wall of rectifier above liquefied O_2 level (gas in equilibrium with liquid O_2)
O.V. Hand operated liquefied oxygen delivery valve, by passing float valve
R.V. Relief valve on high pressure line between filter for solid CO_2 and expansion valve
R.D. Rectifier relief diaphragm
G.X. Pressure gauge before expansion valve
G.R. Pressure gauge to rectifier (0–50 psi)
XV. Expansion valve cover
F.L. Liquid Freon-12 line
F.G. Gaseous Freon-12 line
F.D. Oil drain on Freon interchanger

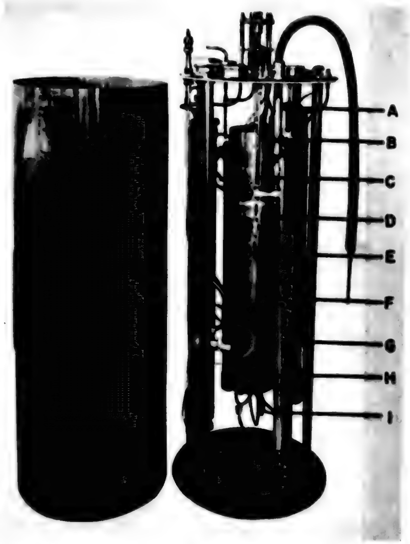


FIGURE 4. Keyes unit, Servel model.

A H.P. O_2 0–3,000 pressure ga.
B. Rectifier 0–50 pressure ga.
C. H P Exp Valve 0–4,000 pressure ga.
D. Air Inlet 0–4,000 pressure ga
E. Liq. Level Ga. 0–5 in. of H_2O
F. O_2 Manifold 0–3,000 pressure ga.
G. Air exch. pump valve
H. Air inlet pump valve
I. Boiler drain valve
J. Gas valve
K. Liquid valve
L. Oil drain

4.3 ARTHUR D. LITTLE-LATHAM UNIT

A second high-pressure unit to produce 20 to 25 lb per hr of liquid oxygen for submarine use was designed, embodying the same thermodynamic principle as the Keyes unit, but incorporating somewhat different heat exchanger, fractionating tower, pressure reducing mechanism and means of insulation. This unit was called the Latham unit.[11,12] Requirements and design were the same as for the Keyes unit. The two most significant differences between the Keyes and Latham units were the method used for expansion and the method used for insulation.

The Latham unit used a capillary tube rather than an expansion valve to allow for the Joule-Thomson refrigeration. The capillary expansion tube was so devised that when plugging by carbon dioxide occurred, it could be thawed out and the plug removed in a very short time by a simple thawing operation. The second most distinctive difference was that the Keyes unit was insulated in the usual manner by glass wool, whereas the Latham unit had all its cold elements encased in an 8-in. diameter steel cylinder with an integral vacuum jacket. The whole cold box was thus contained in a steel cylinder 5 ft high. The flow sheet for the Latham unit is given in Figure 6, and Figure 7 shows the unit itself without jacket. A

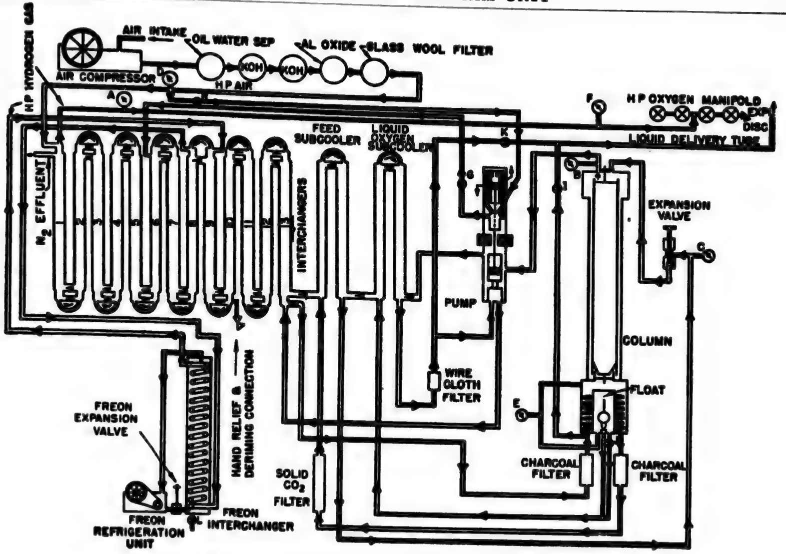


FIGURE 5. Flow sheet of Keyes pump unit, Independent Engineering Co.

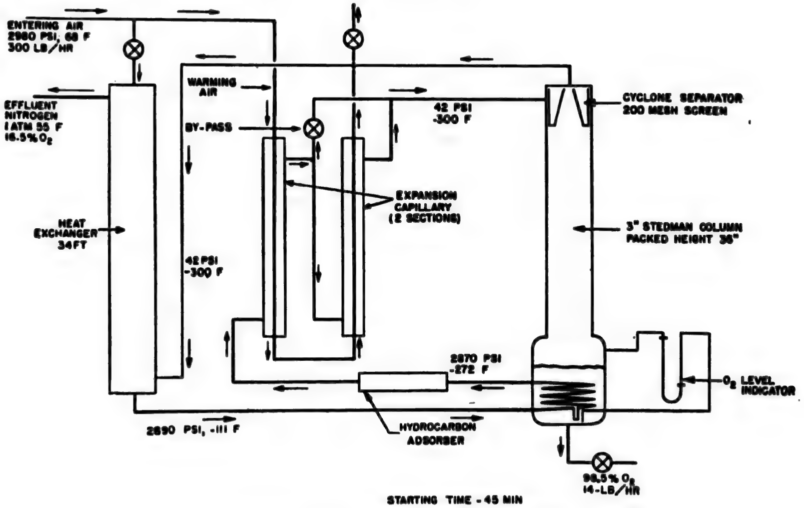


FIGURE 6. A. D. Little—Latham unit, flow sheet.

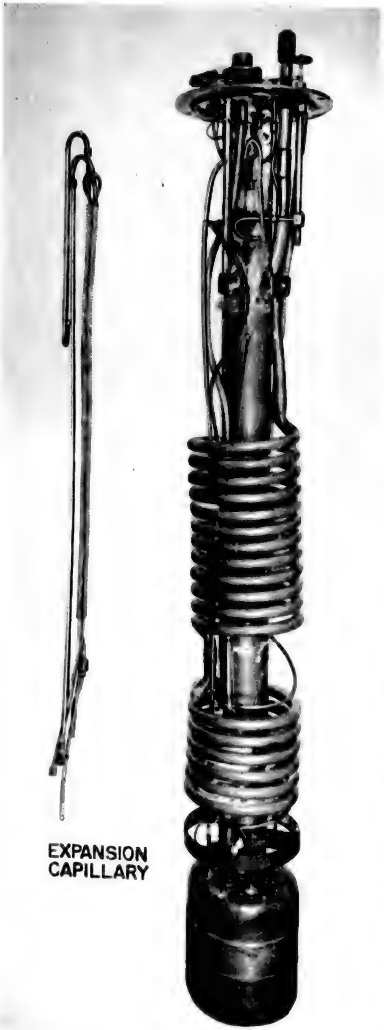


FIGURE 7. The A. D. Little—Latham liquid oxygen unit removed from the vacuum case. The expansion capillary is at the left.

Stedman column was used for fractionation and proved to have a much lower capacity than design called for. The unit operated successfully during several test runs, but it was found that the effective life of the vacuum insulation was rather short and over a six months' period, heat leak through the jacket rose from 80 Btu per hr to about 600 Btu per hr.[6,12] The unit was not developed beyond the testing stage since its production could not be maintained at more than 12 lb of liquid per hr. Purity was obtained only with great difficulty due to the operation of the Stedman tower.

4.4 TRAILER-MOUNTED GIAUQUE LIQUID OXYGEN PLANT—THE GIAUQUE UNIT

A high-pressure plant suitable for both shipboard and trailer mounting was laid out on the cascade refrigeration principle and resulted in the Giauque unit.[13,15] The unit was designed to produce 84 lb of liquid oxygen of 99.5% purity per hr. Its total weight, including trailer and all necessary equipment for operation, was 16,000 lb. It was designed to operate using three refrigerants aside from air, namely, ethane, butane, and nitrogen. The air supply to the unit was 3,000 psi to start, and a lower pressure in the neighborhood of 2,000 psi during continuous operation. Several novel features were employed in the process, aside from the stepwise or cascade refrigeration principle. A flow sheet for the process is given in Figure 8.

A four-stage, high-speed, lightweight air compressor was developed for the plant[10,14,15] (see Chapter 5). The compressed air was taken through an aftercooler and water separator and then passed through potassium hydroxide solution for drying. The warm dry air was then sent to heat exchangers known as refrigeration purifiers, thence to an ethane evaporator. After passing through the ethane evaporator, the air was returned and passed countercurrent to itself in the refrigeration purifier. Thus, dry, warm air was cooled in the refrigeration purifier by the return stream of the same air after having been cooled to approximately −130 F by ethane refrigeration. In this operation the air was chilled to a low temperature whereupon all remaining water and any condensable hydrocarbons were precipitated in the exchanger, hence the term purifier. The temperature of the pure air from the refrigeration purifiers was within a few degrees of the temperature of the entering air. The

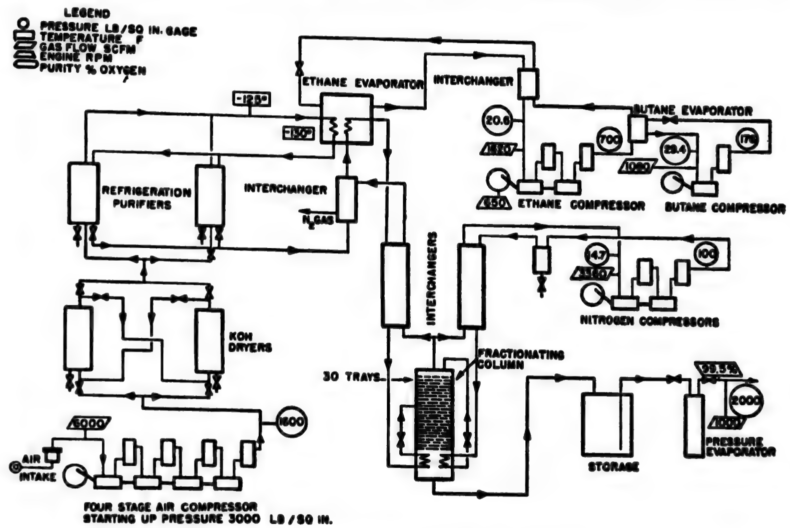


FIGURE 8. Giauque mobile liquid oxygen unit flow sheet.

refrigeration purifiers were switched at suitable time intervals and allowed to thaw for removal of water and hydrocarbons. The dry, clean air from the purifier was then passed through an exchanger countercurrent to effluent nitrogen which was exhausted at this point. The cold air then entered the same ethane evaporator from which the refrigeration purifier obtained its activation. The air leaving this evaporator was at approximately −130 F and then passed through a nitrogen interchanger against the effluent from the fractionating column. This cold air was completely liquefied in the reboiler of the column and allowed to enter the column through a capillary expansion valve. The ethane evaporator was fed with liquid ethane from an ethane compressor operated at a discharge pressure of 700 psi. The ethane was condensed at this pressure by butane which was contained in a separate cycle. The butane compressor operated with a discharge pressure of 176 psi and the gas was expanded to a butane evaporator, extracting its heat for evaporation from the 7 psi ethane. Inlet pressure to the butane compressor was approximately 30 psi. High-pressure cold ethane gas was further cooled by an interchanger using evaporated ethane from the ethane evaporator at approximately 21 psi, which was the intake pressure of the ethane compressor.

Still a third refrigeration machine was planned for the unit. This refrigeration was to be accomplished by nitrogen. The overhead from the fractionating column was to be warmed up by passage through an interchanger, and compressed by a dry nitrogen compressor to about 100 psi. This high-pressure nitrogen passed countercurrent to the nitrogen intake to the compressor, whereupon it was to be cooled to approximate liquid air temperature. The cold high-pressure nitrogen was then to be liquefied in the reboiler of the column and passed through an expansion valve, thereby supplying liquid nitrogen reflux to the top of the fractionating column.

Such a compound refrigeration mechanism constitutes the cascade cycle and results in the most efficient use of energy to produce a given amount of refrigeration. Since the product was to be liquid oxygen, it was highly desirable to develop a system showing the greatest fuel economy. The liquid oxy-

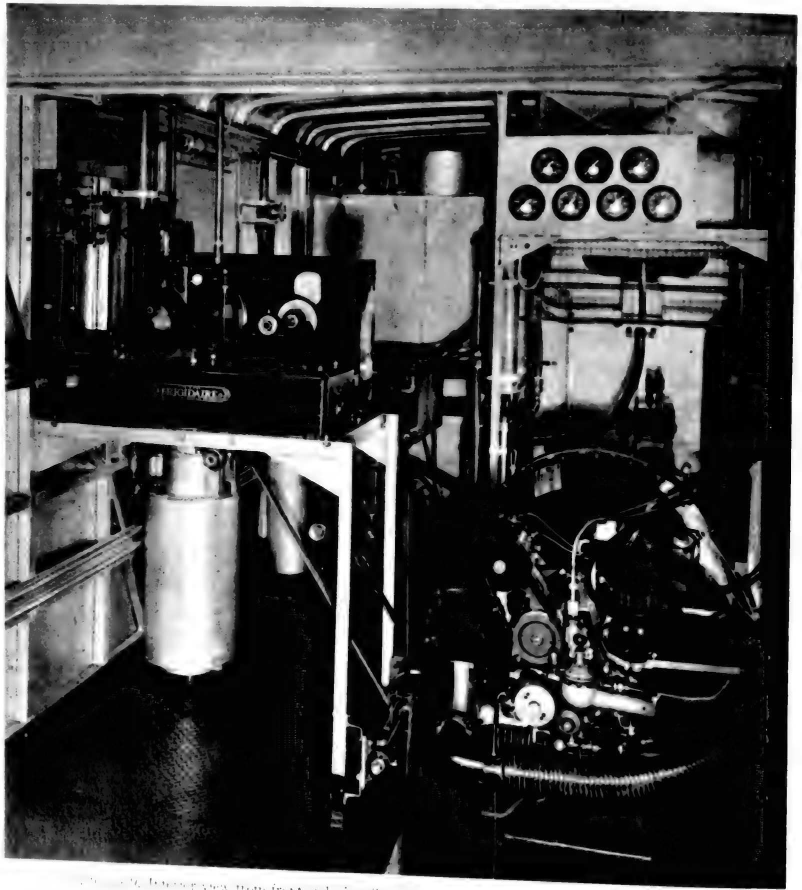


FIGURE 9. Interior view from front end of trailer after installation of air compressor and engine.

gen production, the unit could either be transported in bulk to other sites or to individual vaporizers where it could be vaporized to gaseous oxygen at either high or low pressure.

The dry nitrogen compressor was not satisfactorily developed in time for incorporation in the unit. The final Giauque plant which was built and operated omitted the nitrogen refrigerating cycle but did include the ethane and butane compressors. The unit was also operated with Freon rather than with ethane in the ethane compressor and without making use of butane. Thus, the system could be used either as laid out or with Freon in place of the ethane. The results of these modifications and test runs are cov-

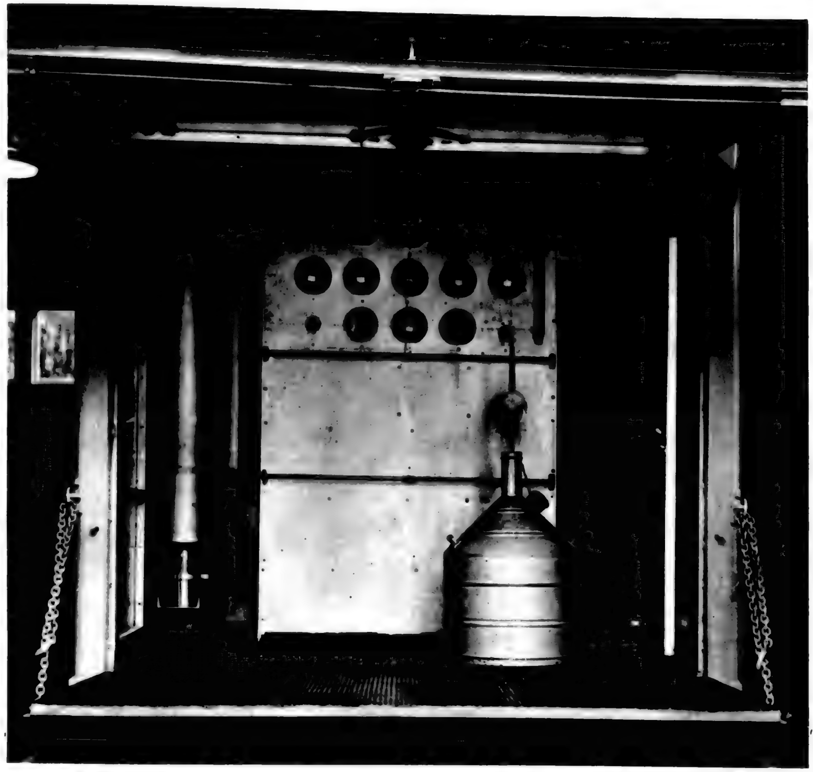


FIGURE 10. Rear platform and operating panel of liquid oxygen trailer unit.

ered in various reports, especially No. 4141. Complete details regarding all equipment, design information, and test runs are given.[16,17] Figures 9 and 10 are pictures of the Giauque unit.

No production models were made as other liquid producing units were available, which operated with a less complex cycle and required fewer service supplies. The unit met design specifications. It was a successful development because it proved the operability of the process. Features of the plant were used in the liquid producing plants which the E. B. Badger Company supplied to the Navy.

4.5 TRAILER-MOUNTED GASEOUS OXYGEN PLANT—THE KELLOGG M-1 UNIT

A plant was laid out on the basis of a process using 3,000 psi pressure air to produce 1,000 cfh of high-purity gaseous oxygen. The plant was trailer-mounted and its total designed weight, including trailer, was 24,700 lb.[19] Figure 11 is a flow sheet of the M-1 cycle. The original intention was to develop a low-pressure trailer-mounted plant and a high-pressure trailer-mounted plant, both to perform

the same service. The M-7 plant was developed and operated successfully some time before the M-1 plant was ready to run. The low-pressure M-7 cycle had many advantages, and after its reliability had been proved, work was stopped on the M-1 plant. The M-1 was never run as a complete unit but the cold box was operated with the use of high-pressure air from standard high-pressure compressor equipment until pressure test failure. The M-1 cycle permits production of gaseous oxygen delivered at high pressure without the use of chemicals for air cleanup. Figure 12 is a view of the trailer-mounted unit showing the compressor, engine, and intercooler equipment.

The following description of essential features of the unit will be useful in understanding its operation in connection with the flow sheet of Figure 11.

The refrigeration required for liquefaction is generated by high-pressure Joule-Thomson or throttling expansion enhanced by Freon forecooling according to the familiar Linde cycle with forecooling. Joule-Thomson expansion is employed in one single stage, and the greater thermodynamic efficiency which is obtainable by stepwise expansion has been sacrificed in favor of simplicity.

Water is removed from the air by condensation, where possible, and by activated alumina. Carbon dioxide is removed by precipitation and filtration, thus making the unit independent of chemical supplies, an advantage of very great value for mobile field units.

The fractionation system embodies two towers, which, contrary to conventional installations, are side by side and not one above the other. Though the conventional tower arrangement means a simpler system, the M-1 system is capable of comparable performance, and its lesser height is a controlling consideration for a mobile unit.

Air Compression. Air is compressed in a high-speed, air-cooled, 6-cylinder, 4-stage air compressor which is driven by a similar high-speed air-cooled Lycoming internal combustion engine. The air is delivered at 3,000 psi during the starting period, but the pressure is dropped back to 800 to 1,000 psi for normal steady operation. After each compression stage the compressed air is cooled in an Aerofin tube section directly against a blast of cooling air supplied by a Sturtevant blower. Means are provided after each stage of the Aerofin cooler to remove condensate from the compressed air.

Water Removal. The compressed air leaving the aftercooler is then cooled by the high-level Freon system to some 20 F below room temperature in order to condense more water from the air and make the duty for the alumina dryers smaller. The C-17 air cooler (see Figure 11) is followed by a drip drum, and then by an air filter, G-9, in order to separate the condensed water from the air.

The air then enters the activated alumina air dryers, G-4. Two dryers are provided so that one may be regenerated while the other is in service. The dryers are regenerated with waste nitrogen from the plant heated to 500 F by means of the engine exhaust. This exhaust heater, B-1, can be by-passed so that cool waste nitrogen may be used to cool the dryers after regeneration. The dryers are set up on a 4-hr operating cycle; 2 hr are allowed for drying, 1 hr for regenerating, and one for cooling. A timer and set of automatic valves have been incorporated into the dryer system so that the drying operation is fully automatic and requires no manual attention from the operators.

Cooling. The dried air leaving the air dryers is then divided into two portions, one of which is cooled against the oxygen from the fractionation system, while the other is cooled against the waste nitrogen and forecooled against Freon from the low-level Freon system.

The smaller portion of dry air enters the oxygen coolers (C-4A and C-4B) in which it is cooled countercurrently with oxygen. The two exchangers are arranged to give an operating air temperature of −121 F between the two exchangers. This is done so that all of the carbon dioxide precipitation which occurs on cooling is concentrated in the C-4B exchanger, which has straight smooth-bore tubes for the air passage, in order to avoid fouling the heat exchanger. The C-4A exchanger has more tortuous air passages, and, though it is a more efficient, compact exchanger, it is more susceptible to fouling with precipitated carbon dioxide. Therefore the combination of exchangers is used in order to get a comp[act] unit, where no precipitation of carbon dioxide [can] be expected, and a unit which will allow precipit[ated] carbon dioxide to pass on to the filter in that port[ion] where precipitation occurs.

The cold air containing carbon dioxide goe[s to] the G-7 filter after leaving the oxygen cooler C[-4B]. The bulk of the air leaving the G-4 air dryers ent[ers] the C-2 nitrogen precooler, where it is cooled aga[inst] waste nitrogen. This air then flows through the [C-...] Freon forecooler, where it is cooled by low-l[evel]

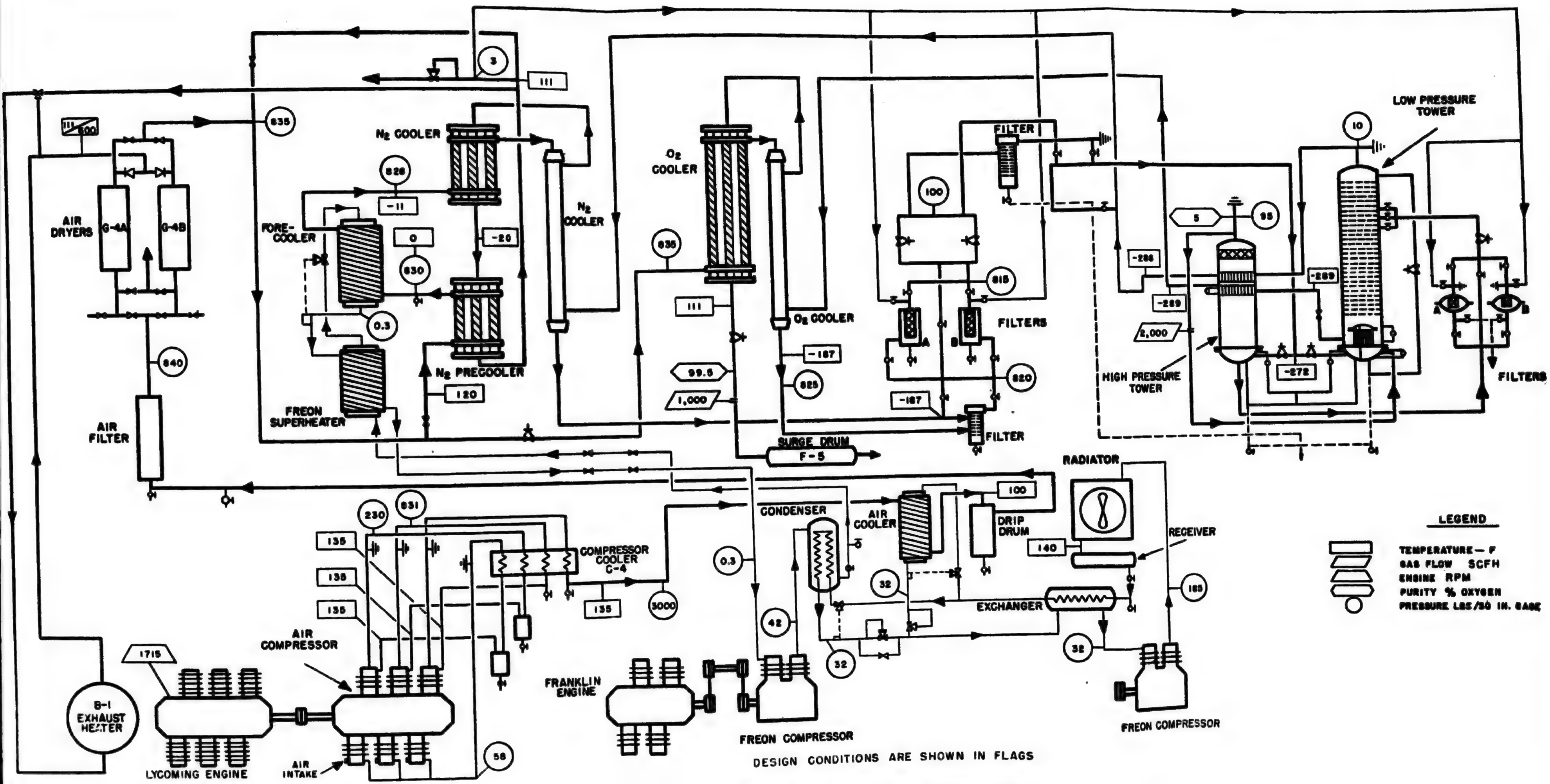


FIGURE 11. The M. W. Kellogg Co. 1,000 cfh mobile oxygen unit, mechanical high-pressure system.

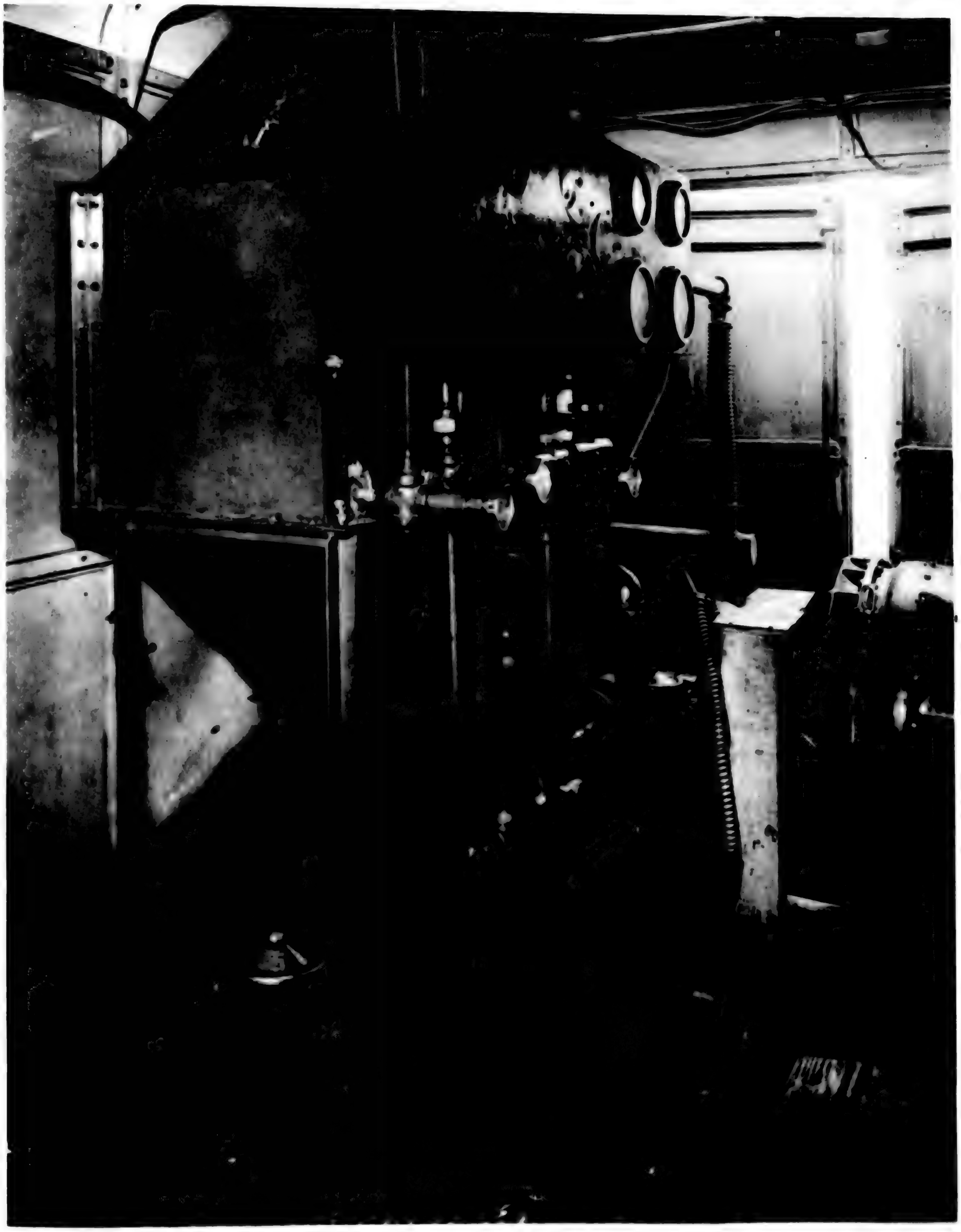


FIGURE 12. Inside the compressor trailer of the M-1 unit. Intercooler and aftercooler in the sheet metal duct with the compressor just beyond. Lycoming engine in right background.

Freon, and then flows through the C-5A and C-5B nitrogen coolers, where it is cooled against waste nitrogen. The nitrogen coolers C-5A and C-5B bear the same relation to each other as do the C-4A and C-4B oxygen coolers, namely the air temperature between these two units is controlled so that precipitation of CO_2 occurs only in the C-5B unit, which is designed to allow the solid phase to pass through to the G-7 filter, but which is not so compact a unit as the C-5A exchanger. The Freon forecooling, which is used to enhance the Joule-Thomson expansion refrigeration generated by the unit, is applied only to the portion of air flowing through the C-1 Freon forecooler.

Filtration of Carbon Dioxide and Expansion of Air. The two portions of feed air, which had carbon dioxide precipitated in the C-4B and C-5B exchangers, come together in the shell of the G-7 filter. This filter has a self-cleaning, rotating Cuno cartridge. Because it is self-cleaning only one such filter is needed, but because its use in this service was experimental, it is followed by the duplicate G-5 filters. These G-5 filters have a glass cloth filtering medium and are provided with thawing connections, so that they can be thawed alternately.

The cold high-pressure air, after filtration, is then throttled from the operation pressure to 100 psi in the expansion valves. The two throttle valves will be used when expanding from the 800-psi operating pressure, but only one valve will be required when throttling from the 3,000-psi starting pressure.

Though the high-pressure air was freed of carbon dioxide snow before expansion, more precipitation occurs on throttling. This snow, formed on throttling, is removed from the air stream in the G-8 filter, which has a self-cleaning, rotary Cuno cartridge.

Fractionation of Air. The throttled, filtered air then enters the fractionation system, which consists of a high-pressure tower and a low-pressure tower. Part of the feed air enters the bottom of the high-pressure tower where it is separated into an overhead pure nitrogen vapor product, and a bottom of rich air liquid product. The refrigeration providing reflux for this tower is supplied by evaporation of liquid oxygen withdrawn from the low-pressure tower, and by heat exchange with the overhead nitrogen from the low-pressure tower.

The overhead nitrogen vapors from the high-pressure tower are condensed in one section of the reboiler of the low-pressure tower, and are then expanded to the top of the tower to be used as reflux for the enriching section of the tower.

That part of the feed air which did not go to the high-pressure tower is condensed in the second section of the low-pressure tower reboiler. This condensed air joins the rich air bottoms from the high-pressure tower and the mixture is filtered in duplicate glass cloth filters, G-1, and then throttled to 25 psia and sent to the low-pressure tower as enriched liquid air feed.

Liquid oxygen is withdrawn from the bottom of the low pressure tower, then evaporates in one of the condenser sections of the high-pressure tower, thus providing reflux. The oxygen vapors so formed give up their refrigeration to part of the incoming air in the exchangers, and emerge at room temperature.

Gaseous nitrogen is taken from the top of the low-pressure tower and is warmed slightly in a second condenser section in the high-pressure tower. The nitrogen then flows through C-5B, C-5A, and C-2, where it is warmed up to room temperature against feed air, but by passes the C-1 exchanger. The dry room-temperature nitrogen is used for regenerating the G-4 air dryers, by being sent through the B-1 exhaust heater to the dryer for regeneration, or directly to the dryer for cooling. The room-temperature nitrogen is also used to thaw the G-1 and G-5 filters.

Compression of Oxygen. The atmospheric temperature and pressure oxygen from C-4A is compressed in four stages to 2,200 psi in a dry carbon-ring, non-lubricated compressor, being cooled after each stage of compression directly against cooling air in an Aerofin tube cooler. The compressed oxygen is filtered and charged into cylinders at 2,200 psi.

Freon System. The prime purpose of the Freon system is to provide forecooling to the feed air in the C-1 forecooler. Freon is vaporized at −20 F and atmospheric pressure in C-1, and the Freon vapors are then superheated in the C-3 Freon superheater before being compressed in the J-4 low level compressor to the condensing pressure. The vapors are condensed in the C-16 condenser at the expense of Freon liquid supplied by the high-level Freon system, and the condensate is subcooled in the C-3 superheater and then expanded into C-1 where it evaporates, supplying the forecooling duty to the process air.

The high-level Freon liquid is condensed in the C-15 air cooled radiator, and is subcooled in the C-8 exchanger. Part of this subcooled liquid is expanded

into the C-16 condenser where it evaporates in order to condense low-level Freon discharged from the J-4 Freon compressor. The rest of the liquid from C-8 is expanded into the C-17 air cooler where it evaporates, cooling the process air and condensing some water out of the air. The high-level Freon vapors from the C-16 condenser and the C-17 air cooler join together, and are superheated in the C-8 exchanger. The superheated vapors are compressed in the J-3 high level Freon compressor and condensed in the C-15 radiator.

A two-level, cascaded Freon system was chosen because it was desired to evaporate Freon at −20 F and cool the Freon system with 120 F ambient air. Under these conditions, the compression ratio was too great to be handled satisfactorily in one stage.

4.6 TRAILER-MOUNTED GASEOUS OXYGEN PLANT—THE AIR REDUCTION COMPANY UNIT

A unit was built for the production of 400 cfh of high-purity gaseous oxygen and was mounted on a single trailer 16 ft long and 8 ft wide. The total weight of the unit, including trailer, was 13,000 lb. It was primarily intended to be a unit which could be assembled quickly from equipment already available to the industry, and for the purpose of charging cylinders for use by the Army Engineers and the Air Forces.[20,21,22] Quick starting time was anticipated and achieved. Figure 13 is a flow sheet of this unit and shows designed conditions for start-up operation. Air pressure can be reduced during continuous operation.

The operation starts at high pressure using a straight Linde system with Freon forecooling using air pressure of 2,000 psi. The high-pressure air passes over caustic potash in cylinders and thence to an alumina dryer. After cleaning, the air passes through an exchanger, is cooled by exhaust nitrogen product oxygen, and thence passes to a Freon forecooler where its temperature is dropped to about −25 F. From here it passes to another exchanger where it is further cooled by product oxygen and tower overhead. The high-pressure air is liquefied in the reboiler, subcooled by nitrogen overhead, and then expanded through a valve into the tower. The exhaust nitrogen is passed back through the heat exchanger system and part of it is used in a nitrogen heater to reactivate the alumina dryers. Oxygen gas from the reboiler is compressed by a three-stage oxygen compressor to 2,000 psi and is then passed over a water separator and drying equipment. The oxygen is dried by alumina which in turn is reactivated by warm dry oxygen heated by hot exhaust nitrogen. Brief specifications for the principal parts of the unit are shown below.

- Fractionation system
  - Plate tower, 6-in diameter, 8 ft long, 24 trays 3⅛-in. spacing.
- Refrigeration system
  - Coiled tubes (5) in shell exchangers. Total surface, 100 sq ft; 4 in diameter by 60 in. Total weight, including forecooler, 250 lb.
  - Freon condensing unit. ¾-hp York unit. Weight, 100 lb.
- Air purification system
  - 3, 4.5 in. ID x 60 in. KOH scrubbers. Weight, 380 lb.
  - 2, 4.5 in. ID x 60 in. alumina dryers. Weight, 250 lb.
- Air compression system
  - Rix three-stage, 50 cfm, 500 rpm, 2,000 psi, vertical air compressor. Weight, 3,500 lb.
  - Air-cooled radiators. Freon cooler to cool air to 90 F.
- Oxygen compression and drying system
  - Three-stage, 6.5 cfm, 250 rpm, 2,000 psia, vertical water-lubricated oxygen compressor.
  - 2–3 in. ID x 30 in. dryers. Weight, 60 lb. Regenerated by oxygen heated by exhaust-heated nitrogen.
- Miscellaneous
  - Ford engine. 1,600–1,700 rpm, 57 hp.
  - Lindsay-structure trailer, 12 x 15 x 11 ft. Weight, 6,000 lb.
- General
  - Starting time, 4 hr at 1,500 to 2,000 psia.
  - Running pressure, 500 to 700 psia.

This unit was operated successfully but severe vibration caused by the air compressor made it desirable to mount the unit on a skid for future experimentation. It formed the basis for the design of a production model built for the Navy by the E. B. Badger Company for liquid production. These production models, however, had additional features such as a packed rotating column which is believed to be advantageous for shipboard operation. Final production models made use of assembly line compressors rather than those used on the Air Reduction model.

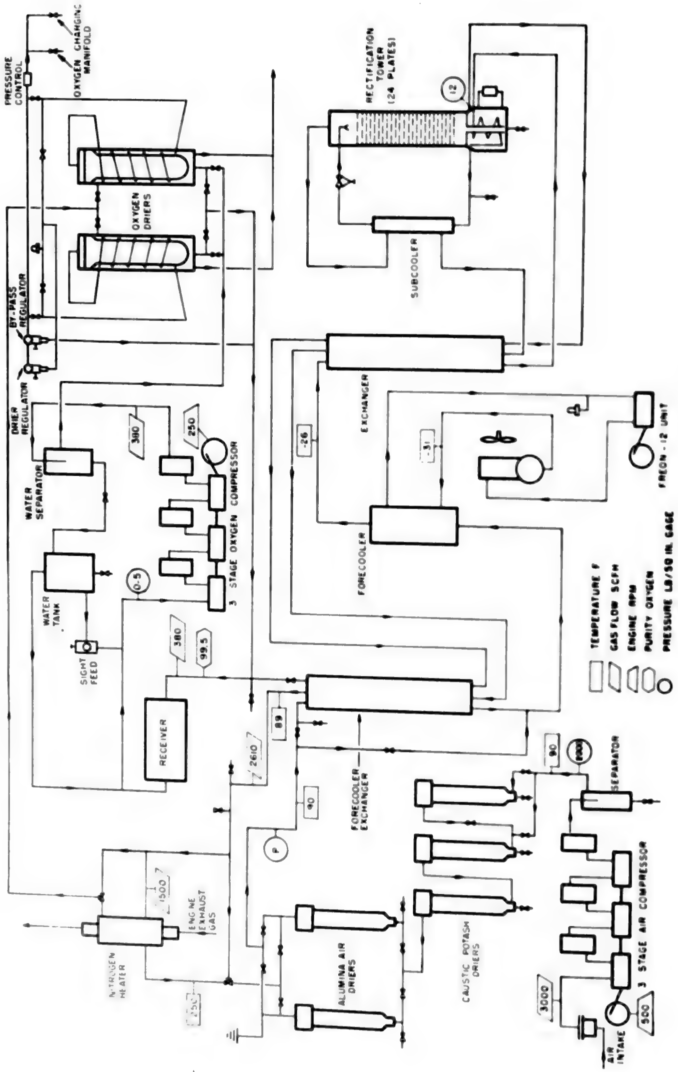


FIGURE 13. Air Reduction Co., Inc., portable oxygen unit

The prototype truck-mounted unit was later dismounted and built on skids, and was revamped to produce liquid oxygen. Also, a liquid oxygen pump was added to compress liquid oxygen (previously vaporized and recondensed) and this eliminated the use of an oxygen compressor and oxygen-drying apparatus.[20] Figures 14 and 15 show the skid-mounted plant.

After improvements, made in the skid-mounted setup, this plant was used in part to provide pertinent information for the large M-6 liquid oxygen plant. Studies in carbon dioxide filtration were carried out in the skid-mounted plant before they were applied to the M-6, and the use of caustic was eliminated by successful adaptation of filters. Details on the skid-mounted plant are as follows.[22]

Column Performance

	Run No. 1	Run No. 2
Air flow, standard cfm	50	70
As gas producer		
Cubic feet oxygen per hour at 99.5% purity	310	440
Cubic feet oxygen per hour at 99.0% purity	350	480
Running pressure psi	1,200	1,000
As liquid producer		
Lb O_2 per hr, air at 1,850 psi (forecooled to −2 F)	....	24
Lb O_2 per hr, air at 2,000 psi (forecooled to −55 F)	....	33
Liquid oxygen purity, %	....	99.5+
Starting time, hr	....	1.5

The above performance at 70 cfm is that of the entire plant as shown, with the exception of the engine and air compressor which are incapable of delivering more than 50 cfm of air. It was necessary to add 20 cfm of air to the compressor output to get the tests at 70 cfm rating.

The forecooler refrigerator used in the setup shown is adequate for the purpose of making gas production at either rate, but is somewhat short of sufficient capacity for best results when producing liquid oxygen.

Refrigerator units

Forecooler, York ¾-hp size, air cooled.

Dehydrator, water-cooled Carbondale ¾-hp size, runs at half speed with back pressure control to hold 32 F on evaporator.

Engine

Ford 95-hp industrial unit as assembled by K. R. Wilson Company, New York, drives all equipment. About 40 hp is used at 1,600 rpm to operate plant at 50 cfm of air flow.

Compressor

Rix vertical three-stage water-cooled 50 cfm at 500 rpm to 2,000 psi.

Operating Supplies Based on 70 cfm Air Flow
(55 to 60 hp required)

	Per 24 hr operation	Per 1 week operation
If diesel drive		
Diesel oil, lb (based on Caterpillar D4600)	680	4,100
If gasoline engine drive		
Gasoline, gallons	140	980
(based on Ford consumption) lb	840	5,880
Potash, lb	10	70
Engine oil, gallons	½	3½
Compressor oil, gallons	⅛	1

Approximate Weights

Skid plant as shown in Figure 14	Pounds
Column skid, including column and liquid pump	2,500
Potash tube—dryer skid	1,000
Refrigeration unit skid	400
Ford power unit	1,400
Rix compressor	4,000
Total	9,300

4.7 PORTABLE UNIT FOR EITHER LIQUID OR GASEOUS OXYGEN PRODUCTION—THE LEROUGET PLANT M-31

A plant was built on the basis of a high-pressure cycle employing low-level refrigeration by direct air expansion and high-level refrigeration by nitrogen expansion in an expansion engine (Figure 14). This cycle, known as the LeRouget cycle, had been built and operated in Great Britain, but was not tried out in the early stages of the oxygen program. It was later built in the Central Engineering Laboratory of this section in the early part of 1944 and was designed to produce 50 lb of liquid oxygen per hr.[5,10,19] It was visualized that this cycle offered the best possibility for efficient production of either liquid or gaseous oxygen of high purity. Such a unit was coming to be of interest to the Air Forces because it was felt that if liquid oxygen could be produced and stored at times when empty gas cylinders were not available, considerable time could be saved and convenience attained in aircraft oxygen supply. Furthermore, although the Air Forces was committed to the use of gaseous oxygen, it was becoming increasingly apparent that liquid oxygen could and should eventually be the means for using oxygen aboard aircraft. In addition to the desirability of developing an efficient plant for the production of

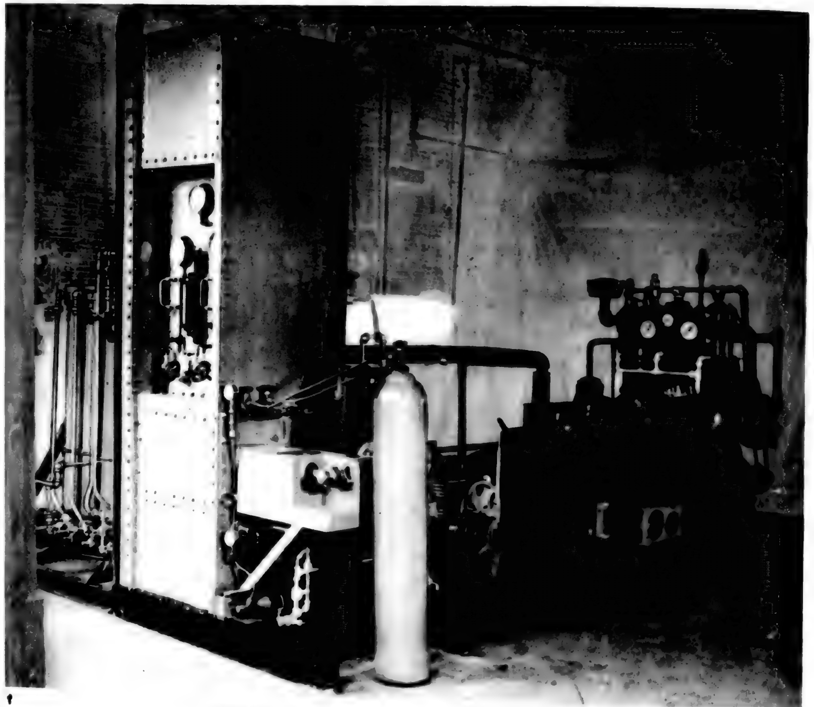


FIGURE 14. Air Reduction Co., Inc., skid mounted unit.

liquid oxygen or gaseous oxygen (with the aid of a liquid oxygen pump, thus eliminating the use of a gaseous oxygen compressor), there were two other objectives in mind. First, to demonstrate the LeRouget cycle as a practicable method for generating liquid oxygen; and second, to develop a system for the mechanical removal of water and CO_2 from the compressed air used in a high-pressure oxygen generator. The first objective was definitely reached, and the second objective approached closely enough to justify the hope that it can be attained after a reasonable amount of further experimentation.

The distinctive feature of the LeRouget cycle is the use of expansion engines in the effluent nitrogen stream to produce a portion of the refrigeration. The remaining refrigeration is obtained by Joule-Thomson expansion of the high-pressure air. Auxiliary forecoolers and heat exchange between the forecooler and the warm air stream are eliminated. To obtain refrigeration from the expansion engines, the fractionating tower, including the low-pressure tower of the double column, must operate at an appreciable back pressure. In the laboratory unit the pressure on the tower was about 50 psi. The high tower pressure leads to two minor disadvantages: the fractionation per tray is somewhat reduced, and if liquid oxygen is made, it suffers a flash loss of approximately 6%. If the unit is operated to produce high-pressure gas directly, and it can be built to do so if a liquid pump is installed, there is no flash loss. The additional fractionation called for by the high distillation pressure can be supplied by a few additional trays.

The unit built and operated in the Central Laboratory at first was equipped with a single tower.

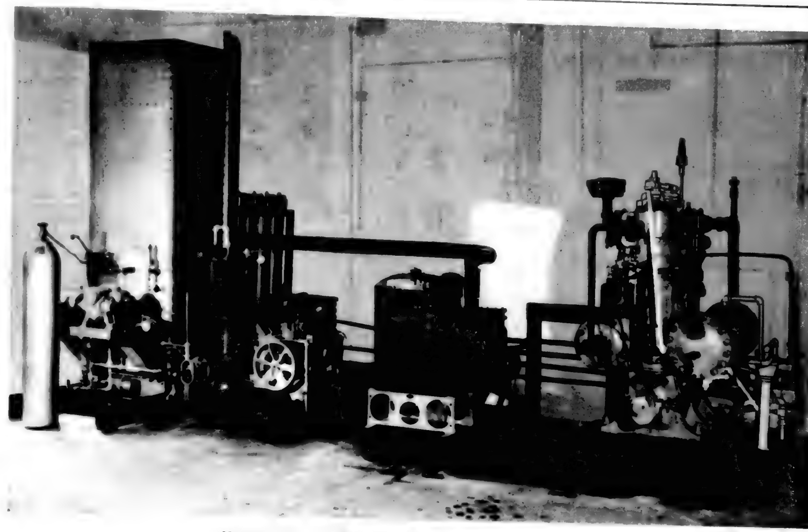


FIGURE 15. Air Reduction Co., Inc., skid mounted unit.

Satisfactory cycle operation was obtained, and then a double column was installed to increase the yield and production of oxygen without increasing the amount of air supplied to the unit. The unit was not equipped with its own compressor, and air at 3,000 psi was taken from laboratory supply service.

A LeRouget cycle is ideal for application of the small, high-speed, rotary expander described in a later chapter. The small expander can only operate on clean gas, and the nitrogen effluent of the LeRouget cycle is completely free of water, oil, and CO_2. Also, the temperature level of the expansion step (-45 to -100 F) is warmer than that in the low-pressure units described in Chapter 2. Because of the higher temperature, lubrication of the expander becomes easier.

The operation of the M-31 unit was very successful as far as the cycle and process were concerned.[10] All operating difficulties originated in the CO_2 cleanup system. As long as CO_2 could be rejected by the unit, operation was smooth and regular. The liquid production rate was 43 lb per hr of 99.4% oxygen, after flash, from 408 lb per hr of air. A flow sheet showing operating data is given in Figure 16.

The mechanical cleanup of H_2O and CO_2 in the unit is accomplished by the following method. The water is precipitated as ice in switching exchangers. The ice is collected in one exchanger, which is derimed when the other exchanger is put into service. The exchangers are switched on a three- or four-hour cycle. No trouble with water removal was experienced during many hours of operation and this portion of the mechanical cleanup system is entirely satisfactory.

The removal of CO_2 mechanically in the M-31 unit proved to be more difficult, and much experimental work has been done to find a solution to the problem. The elements of the solution are at hand, as the last run lasted 200 hr and was terminated by a plugged line.

The CO_2 removal method is based on the filtration of solid CO_2 from the various liquid, or partially liquid, streams that enter and leave the double fractionating column. The septum used in the filters is AA Fiberglas, a new development in glass, which is a felted cloth consisting of very fine (0.5 μ) glass fibers. Several layers of the material can be used without appreciable pressure drop, and the material will remove particles as fine as are present in cigarette smoke. The main problem in constructing the

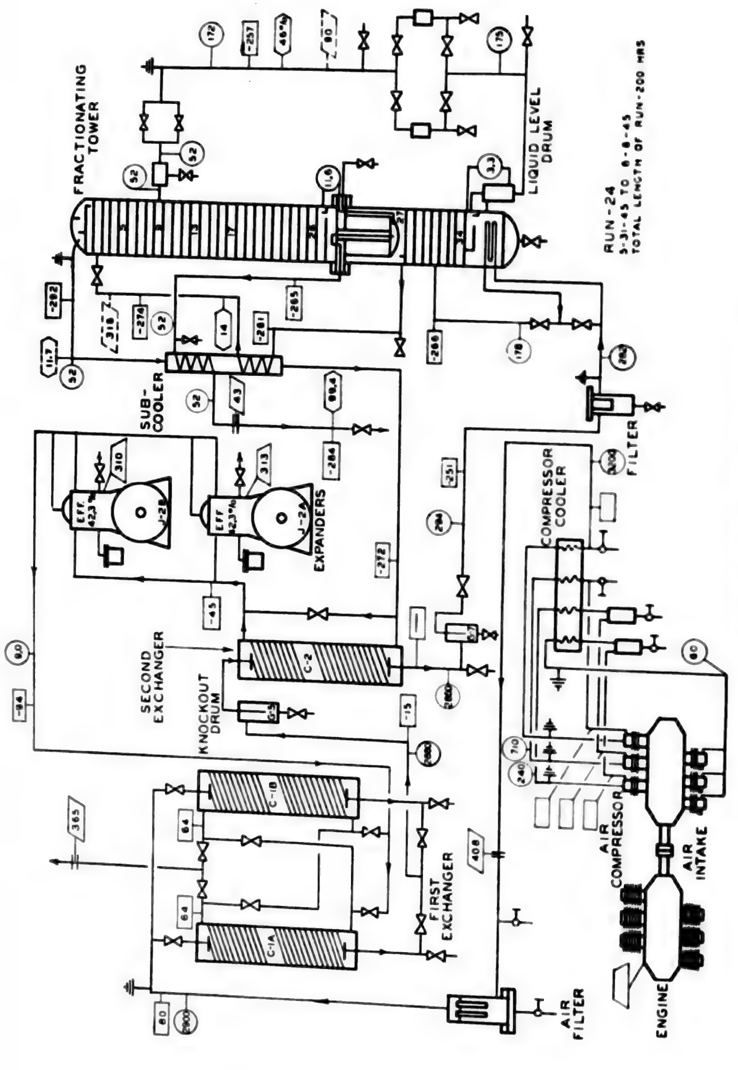


FIGURE 16. Central Engineering Laboratory liquid oxygen unit M-31.

filter is to seal the Fiberglas at the ends of the filter so that particles of CO_2 cannot short-circuit. This problem has not been completely solved.

From the results obtained thus far on solid CO_2 equilibrium with air,[10] in which the dew points of CO_2 in high-pressure air have been measured, it appears that the high-pressure air at 3,000 psi does not precipitate CO_2 in the M-31 unit during the cooling step. At the Joule-Thomson expansion, however, where the pressure is suddenly reduced from 3,000 psi to 300 psi, copious precipitation of CO_2 occurs, both from the reduction of pressure and from the reduction of temperature. A filter (G-2) immediately following the throttle valve removes the CO_2 precipitated in the expansion. Approximately 90% of the CO_2 is removed in the filter. The air leaving filter G-2 is partially liquefied, and liquefaction is completed in the reboiler of the high-pressure tower. In the high-pressure tower the feed is split into liquid bottoms, or rich air, and liquid nitrogen reflux for the low-pressure tower. Since the latter stream is condensed from the vapor phase, it contains no CO_2, and the CO_2 remaining in the air after the filter G-2 is concentrated several-fold in the rich air. The concentration in this stream exceeds solubility, and the excess precipitates in a form that tends to accumulate on the walls of the pipes and in fittings and valves. Accordingly, a second filter, built in parallel duplicates, is installed in the rich air line. These are the G-3 filters. Finally, when the pressure on the rich air is reduced to the pressure existing in the low-pressure tower, additional CO_2 is deposited, which is prone to plug the throttle valve and the pipe leading from the valve to the tower. A third filter, labeled G-6, has been inserted in this line.

With all the filters in operation, a successful run of 200 hr has been made. The run terminated, however, when a plug formed in the line between the main expansion valve and the pressure reduction valve in the line from the high-pressure reboiler.

The mobile oxygen plant of the future may well be an M-31 type of unit, using a diesel-driven, direct piston connected, high-pressure air compressor, a liquid oxygen pump, small rotary expanders, and utilizing the method of mechanical cleanup as just described. Such a unit should be extremely attractive as a small, lightweight, efficient unit capable of producing high-pressure gaseous or liquid oxygen.

Figure 16 gives the flow sheet and operating conditions for a 200-hr run. Production and all other pertinent data are indicated on the flow sheet. The plant has had many hours of successful continuous operation and has also demonstrated its ability to operate intermittently over extended periods of time.[7,8,9,10] Figures 17 and 18 are pictures of the M-31 unit without the high-pressure air compressor.

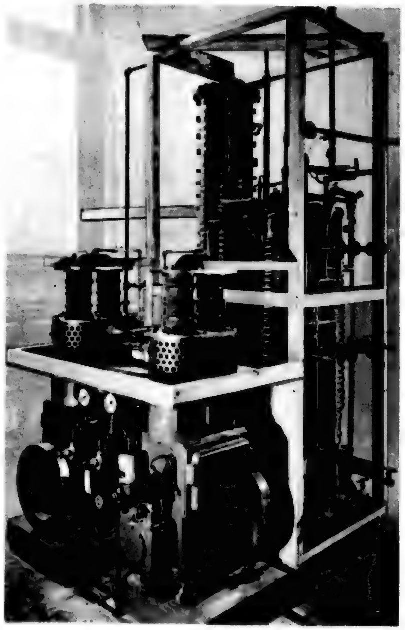


FIGURE 17. M-31 construction. Expander installation.

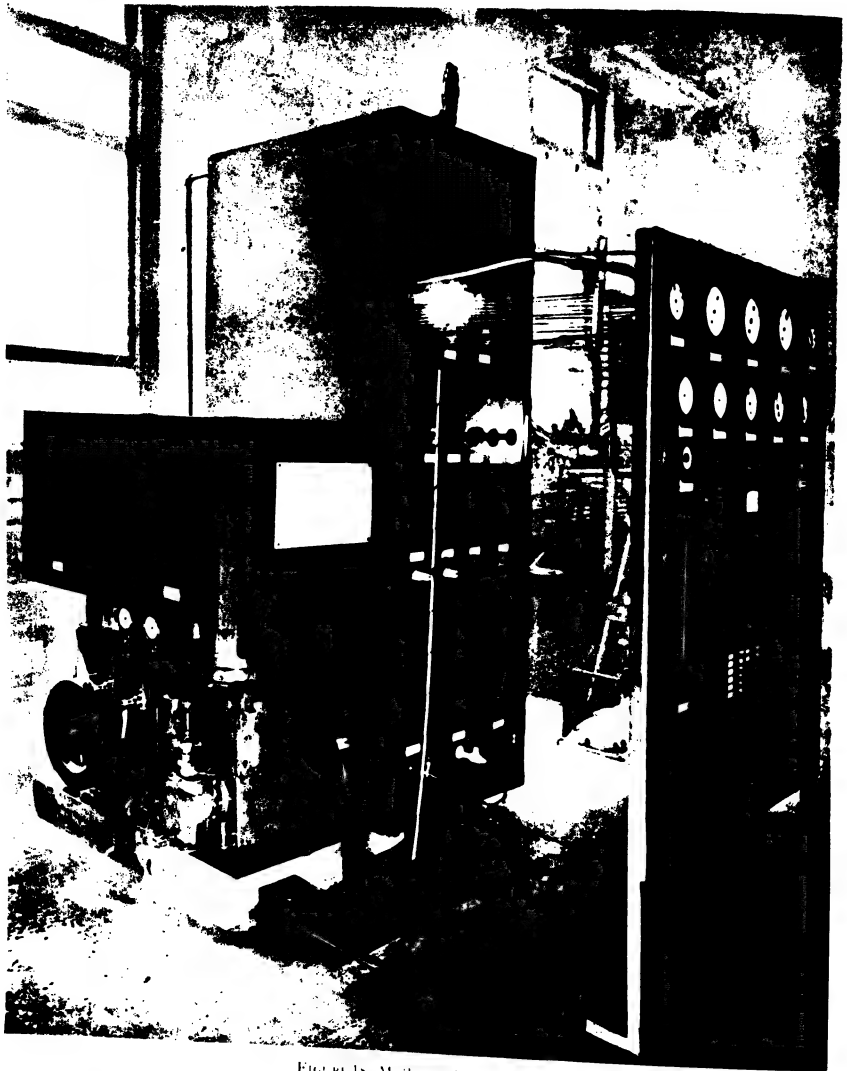


FIGURE 18. M-31 completed unit.

Chapter 5

AIR COMPRESSORS AND EXPANSION ENGINES

By *J. H. Rushton*

5.1 THE COMPRESSOR PROGRAM

An investigation was made to determine whether any standard machines were available for air compressors which would have a very low weight capacity ratio. This survey work took into account all types and sizes of reciprocating air compressors, water-cooled and air-cooled, oil- and water-lubricated, and portable and stationary equipment.[1,2,11,12,16,17,19,23] For compressors under 100 hp and working at discharge pressures not over 300 psi (the so-called portable or small units), it was found that the weight to displacement ratio averaged 13.31 lb per cfm and covered a range of 3.27 to 30.0 as shown in Table 1. Very little difference was found in operating efficiency as judged from published information; the air-cooled units, although lighter, did require more energy output. No equipment found in this class utilized the crosshead-type design, a prerequisite to operation with controlled lubrication or even oil-free operation. More important, no equipment was found for operation with either water as lubricant or else no lubricant at all. (Exceptions to this were two manufacturers' lines of heavy horizontal stationary low-pressure units using carbon rings and water lubrication.)

TABLE 1. Tabulation of various stock compressors.*

Manufacturer	Design discharge pressure	Piston diplacement cfm	Weight	Lb cu ft displacement per min	Comments
Worthington	100	83	900	11.1	
Worthington	100	445	2,700	6.06	
Gardner Denver	100	32	330	10.0	
Gardner Denver	100	367	2,510	6.8	
Curtis	100	9.8	135	13.6	
Curtis	100	53	425	8.0	
Ingersoll-Rand	100	6	180	30.0	Estimated
Ingersoll-Rand	100	52	800	16.	Estimated
Quincy	100	23	275	12.	
Quincy	100	80	525	6.5	
Davey	100	133	555	4.16	
Davey	100	443	1,500	3.40	
Schramm	100	124	600	4.85	
Schramm	100	601	1,960	3.27	
Clark	100	296	500	1.7	(Clark proposal)
Worthington	250	7.7	190	25.0	
Worthington	250	67.0	730	10.9	
Ingersoll-Rand	250	6.5	200	31.0	
Ingersoll-Rand	250	41	600	14.0	
Quincy	250	5	140	28.0	
Quincy	250	22	270	12.3	
Gardner Denver	250	40	750	18.8	
Gardner Denver	250	92	1,650	17.4	
Clark	250	190	500	2.63	(Clark proposal)
Worthington	500	6.1	185	30.0	
Worthington	500	80	1,025	12.8	
Ingersoll-Rand	500	7.4	250	34	
Ingersoll-Rand	500	15.2	520	34	
Quincy	500	4.2	140	33.5	
Quincy	500	20.8	270	12.9	
Clark	600	190	600	3.13	(Clark proposal)
Ingersoll-Rand	1,000	29	660	23	4¼ x 1¼ x 4, Type 20
Ingersoll-Rand	1,000	50	825	16.5	
Rix	1,000	15	550	36.0	

* Data taken from manufacturers' catalogs, 1941.

Turbo or centrifugal compressors were found to be available in extremely high-capacity, low-ratio units, that is, 5,000 cfm operating at a maximum ratio of compression of 3.0. One manufacturer stated that given two years, he could develop a unit having a capacity as low as 3,000 cfm for an overall ratio of 7 in a multistage unit.

Rotary compressors of the type known as displacement blowers were found to be limited in compression ratio, inefficient, and unsatisfactory for our purpose. A type of modified rotary compressor, wherein actual internal compression took place, was found to hold great promise. This compressor, known as the Lysholm type, was then being manufactured in large sizes in this country under foreign licenses by the Elliott Company of Jeannette, Pa. It was thought that a machine of this type could be developed in a two-stage unit having a capacity of as low as 200 cfm for an overall ratio of not more than 6, although this size would probably be the smallest practical unit, according to the designers, and would require considerable development work.

Summing up, there was found to be no commercially available compressor which would meet the following specifications:

Capacity, approximately 200 cfm.
Discharge pressure, approximately 100 psi.
Weight, not more than 700 lb.
Lubrication, controlled or non-lubricated.

It was thought likely that a compressor could be developed for these specifications along either of two lines: a rotary Lysholm type or a two-stage, air cooled, high-speed, crosshead-type, reciprocating machine.

For high-pressure service as required by the high pressure Giauque unit (Chapter 4) there was nothing available in lightweight equipment to meet the following desired specifications:

Capacity, approximately 110 cfm.
Discharge pressure, approximately 3,000 psi.
Weight, not more than 800 lb.
Lubrication, oil.

A development program was initiated to produce a compressor for such service.

As a result of this survey for the requirements of the projected service units, it was decided to design and build the air compressors described in Table 2.[5,10,11]

TABLE 2. Air compressors.

Description	Capacity, cfm	Pressure, psi	Projected weight without drive, lb	Size
6-cylinder reciprocating oil, lubricated, air-cooled, 55 hp	200	90	600	33 x 30 x 24 in.
6-cylinder, reciprocating non-lubricated, air-cooled, 50 hp	200	90	650	36 x 30 x 24 in.
Rotary, high-speed (Lysholm) oil-cooled, 60 hp	200	90	50	24 x 18 x 12 in.
6-cylinder, reciprocating oil-lubricated, air-cooled, 60 hp	100	3,000	600	33 x 30 x 24 in.
4-cylinder, reciprocating combination engine and compressor	35	150	420	33 x 30 x 25 in.
Vertical, low-speed reciprocating diesel-driven, 500 hp	2,000	90	...	12 x 9 x 4 ft
Vertical, medium-speed, diesel-driven, 500 hp	1,000	600	...	12 x 12 x 4 ft

5.2 SIX-CYLINDER LOW-PRESSURE OIL-LUBRICATED AIR COMPRESSOR

An air compressor was desired with a capacity of 200 cfm delivered at 90 psi for use with the 1,000 cfh oxygen plants. Since these plants were to be mounted on trucks, it was desirable to have a compressor of as light weight as possible. The power for such a compressor was felt to be best obtained by the use of aircraft engines of the Franklin or Lycoming types. These engines were also in use by the Services for tanks and other field uses. The speed of such a power device made it desirable to develop a compressor that could be directly connected or at most to have but a small speed reduction from that of the prime engine. The crankcase of a commercial aircraft engine was used as a basis for the compressor. A number of these models were built but they never entered commercial production because of the development of the dry air compressor, which was built on the same principle as this one, except that oil lubrication was eliminated by the use of carbon rings. This oil-lubricated compressor development proved to be extremely useful as a background for the final nonlubricated air compressor to be described next.[11]

TABLE 3. Specifications 4⅞ in. x 4 in. two-stage six-cylinder horizontal opposed oil-lubricated Clark air compressor.

Compressor end		
Design operating conditions		
Gas to be compressed	Air	
Quality	Saturated at 14.7 psia and 95 F	
Maximum suction temperature F	120	
Suction pressure psia	14.7	
Discharge pressure psia	104.7	
Staging data	*First*	*Second*
Suction temperature F	120	140
Suction pressure psia	14.7	36.7
Discharge pressure psia	41.7	104.7
Discharge temperature F	300	325
Dry volume scfm	189	189
Wet volume scfm	200	193
Inlet cond. cfm	223	89.1
Compressor specifications		
Type	Air-cooled horizontal opposed	
RPM	1715	
Stroke in.	4.0	
BHP required	59.0	
No. of compressor cylinders	6 single-acting	
Type cylinders	Finned chrome-plated bore	
Type cooling	Air forced ventilation	
Type piston	Crosshead guided	
Rings	American hammered metallic	
Stage	*First*	*Second*
No. of compressor cylinders	4	2
Bore in.	4.875	4.875
Stroke	4.0	4.0
Piston displacement cfm	296	148.0
Approx. vol. eff.	75.3	60.1
Est. capacity cfm inlet	223	89.1
Est. capacity scfm wet air	200	193
Overall length	33 $\frac{3}{16}$ in.	
Overall width	43 in.	
Overall height	24 in. max.	
Weight complete, less frame	650 lb	
Horizontal distance required to pull compressor pistons from CL of compressor	Cylinder must be removed first 25 in. from CL required	
Accessories supplied		
Intake air filters low stage	4	
Manifold low-stage discharge	1	
Manifold high-stage inlet	1	
Manifold high-stage discharge	1	
Shaft half coupling (Thomas)		
Cooling air shrouding		
Flywheel Fan		
Air filters Crosshead breathers	6	
Mounting supports and mount		

air compressor.[1] The compressor specifications are given in Table 3. Figure 1 shows the resulting compressor with direct-connected drive. Figures 2 and 3 are experimental characteristic curves for this compressor.

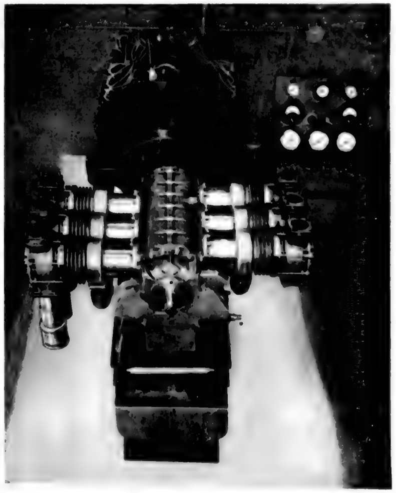


FIGURE 1. Clark 4⅞ in x 4 in., 6-cylinder, 2-stage, "oily" air compressor driven by Franklin engine.

3.5 LOW-PRESSURE DRY AIR COMPRESSOR

This compressor was built on a Lycoming engine crankcase such as was used for tank propulsion. In its final form it was used for the low-pressure mobile 1,000 cfh oxygen plants (M-7, M-7AT, and the LP plants), and a number of these compressors were manufactured by Clark Bros. Inc. Figure 4 shows this dry air compressor, and in Table 4 are the principal specifications. Specifications regarding capacity and stage data are the same as for the oil-lubricated compressor described in Table 3.

It is of a special interest to note that this machine gives very long life, running without lubrication, and the carbon rings are capable of standing severe operating speeds of 1,030 ft per min corresponding to a crankshaft speed of 1,600 rpm. These nonlubricated machines have run under test for continuous operating periods of 150 hr, and have operated for upwards of 1,000 hr before complete overhauling. Conventional oil-lubricated compressors usually operate at piston speeds of 800 ft per min. Using the higher speed in this machine has enabled the realization of a

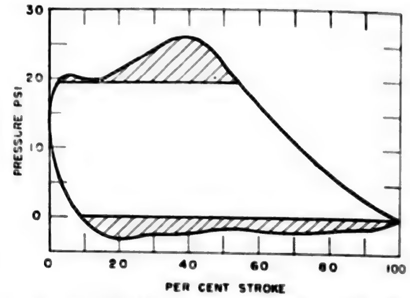


FIGURE 2. Clark 4⅞ in x 4 in., 2 stage, horizontally opposed air compressor, 1,750 rpm.

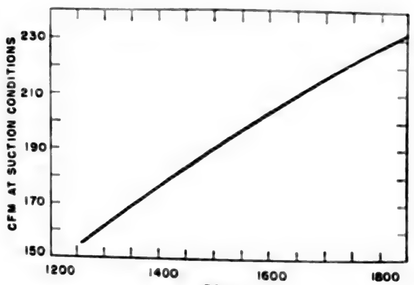


FIGURE 3. Horizontal opposed 4⅞ in x 4 in., 2-stage compressor, capacity vs rpm 90 psi discharge pressure.

low weight per unit capacity of 3.7 lb per cu ft per min discharge.

Complete details regarding construction are covered in various progress reports.[3,4,5,6,8] Probably the most important development in the design of this compressor has to do with the compressor cylinder. Its construction is illustrated in Figure 5.

Performance tests were run at various crankshaft speeds between 1,000 and 2,000 rpm and discharge pressures between 40 and 120 psi. (Figures 6 and 7.) The compressor was designed for 220 cfm and this was attained at 1,600 rpm. (Figure 8.) The maximum speed at which the compressor should operate is 1,850 rpm with a maximum discharge pressure of 110 psi. Pressures in excess of 110 psi result in discharged temperatures which are too high for long valve life. Further, for higher speeds and pressures the bearings are loaded beyond their design. Oil-

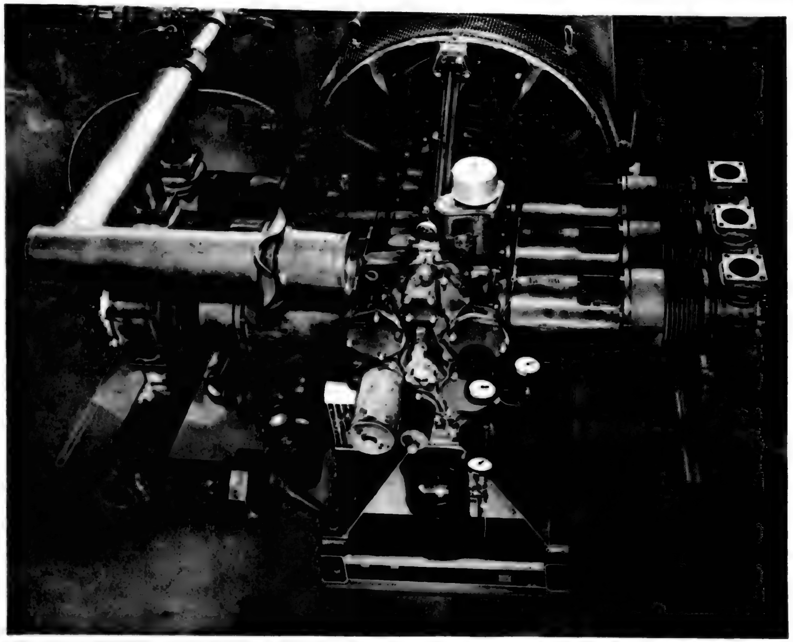


FIGURE 4. Six cycle, two-stage, low-pressure, dry air compressor.

TABLE 4. Specifications Model DH0-6-2 Clark Dri-Air compressor.

Type:	6-cylinder, two-stage, horizontal opposed cross-head nonlubricated	
Model:	DH0-6-2	
Stages	*First*	*Second*
No. of cylinders	4	2
Bore	5 ¼ in.	5 ¼ in.
Stroke	3 ⅞ in.	3 ⅞ in.
Inlet pressure psia	14.7	33.0
Discharge pressure psia max.	35.0	114.7
Discharge temp. F	255	345
RPM	1600	
Capacity at inlet conditions	224	
BHP required	61	
Material specifications		
Cylinders	Highly polished chrome-plated C.I.	
Pistons	Aluminum castings	
Piston rings	3-segment Graphitar #2 (butt joint)	
Guide rings	3-segment Graphitar #2 (butt joint)	
Dimensions		
Installation drawing	108-288	
Overall height	39 ¼ in.	
Overall length	41 ¼ in.	
Overall width	60 in.	
Weight	900 lb	
Equipment supplied	Oil pressure and temperature gauges, oil filter, "one shot" lubricator, air intake filters, and interstage manifolds	

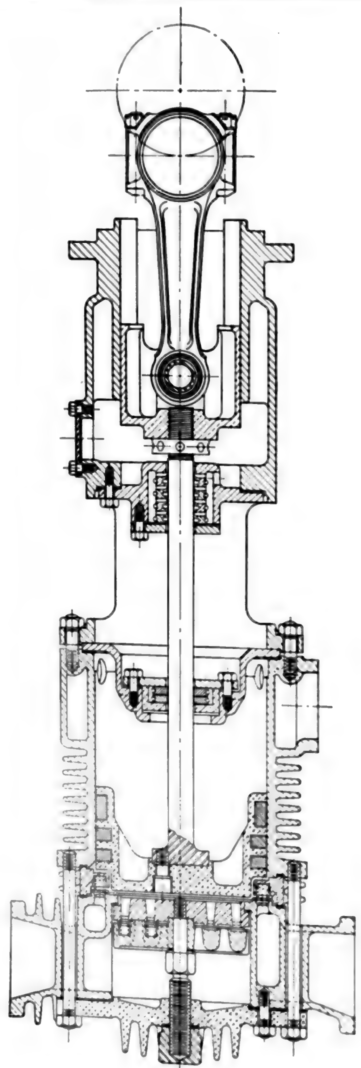


FIGURE 5. Cross-section compressor cylinder Clark Dri-Air compressor.

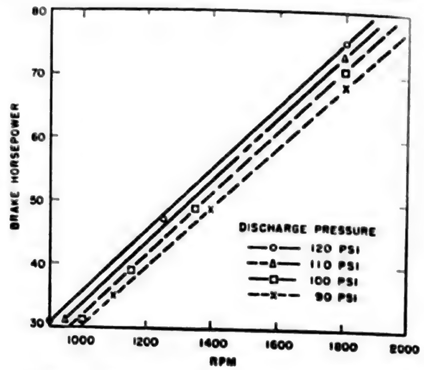


FIGURE 6. Two-stage Dri-Air compressor—speed vs horsepower.

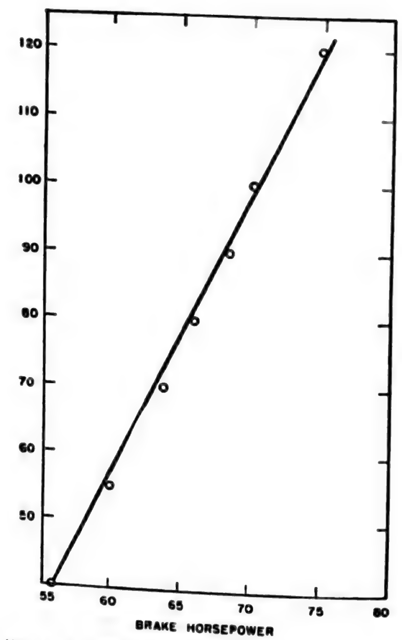


FIGURE 7. Two-stage Dri-Air compressor—discharge pressure vs horsepower.

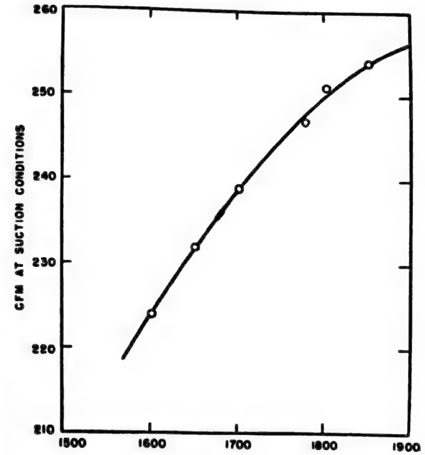


FIGURE 8. Two-stage dry compressor—capacity vs speed; 100-lb discharge pressure suction conditions.

cooling temperature should not exceed 200 F. Although the machine has operated with unexpectedly long life for carbon rings at the severe operating speeds, there is still a lot of further development which should be done to increase the life of the unit and allow it to perform more efficiently. It is anticipated that this machine could be developed to a much higher degree than in its present form. Power requirements for the compressor at different speeds and at different discharge pressures are shown in Figures 6 and 7. Further attention to the details of construction of the carbon rings and guides would undoubtedly result in a decrease in power requirements. The power requirements for the nonlubricated compressor are considered to be modest, considering the weight and portability features of the unit when operating at a discharge pressure of 100 psi and 1,600 rpm. While compressing 224 cfm, the brake horsepower is 61 hp.

5.4 ROTARY TWO-STAGE ELLIOTT-LYSHOLM AIR COMPRESSOR

In an attempt to achieve extreme compactness and lightness in weight, considerable attention and experimentation was given to the Lysholm-type rotary compressor.[9,18,19,20,21] Such a compressor was laid out to have a capacity of 200 cfm of air at one atmosphere pressure and 60 F delivered at 90 psi. Such a compressor was to be nonlubricated and to run at high speed, being direct-connected to a gasoline-driven engine or, if desired, to an electric motor. The total weight of such a unit was anticipated to be approximately 150 lb with the intercoolers. Such a machine was built, tested, and operated for a short period of time and was finally delivered to the Navy Department, Bureau of Ships, for use in the Engineering Experiment Station in Annapolis.[34] The final unit was somewhat cramped in design and the Elliott Company, builders of the unit, felt that the compressor should be redesigned to allow a little more room for bearings and other mechanical elements so that it would not be operating at such critical limits as in this first development model. It was felt that redesign of this nature would be necessary before the unit should be produced in quantity for use by the Services. At the time this decision was reached (July 1944), it was considered inadvisable to continue the development inasmuch as 8 to 10 months' time was estimated before an improved model could be built and that this would be too late to be of use in World War II.

A description of the unit follows.

Design Operating Conditions

200 cfm of dry air at 14.7 psia and 60 F
Suction temperature, 1st stage: 120 F
Suction temperature, 2nd stage: 120 F
Suction pressure: 1 atm abs
Discharge pressure: 90 psi
Gas to be handled: Air
Moisture content of inlet air: Assume saturation at 14.7 psia, 90 F

An assembly drawing of the original design is shown in Figure 9, and Figures 10 and 11 show photographs of the complete unit and rotors as finally assembled.[9]

The compressor is of the Lysholm type with two stages. Both stages are connected to a common drive shaft through a gear case built as an integral part of the unit. The two stages are of identical design, except for length and rotational speed. The high-pressure stage is 0.86 times the length of the low-pressure stage and turns at half the speed (10,000 rpm), giving a displacement of 115.2 cfm as compared with the low-pressure displacement of 297.2 cfm.

The input shaft turns at 2,000 rpm, driving two

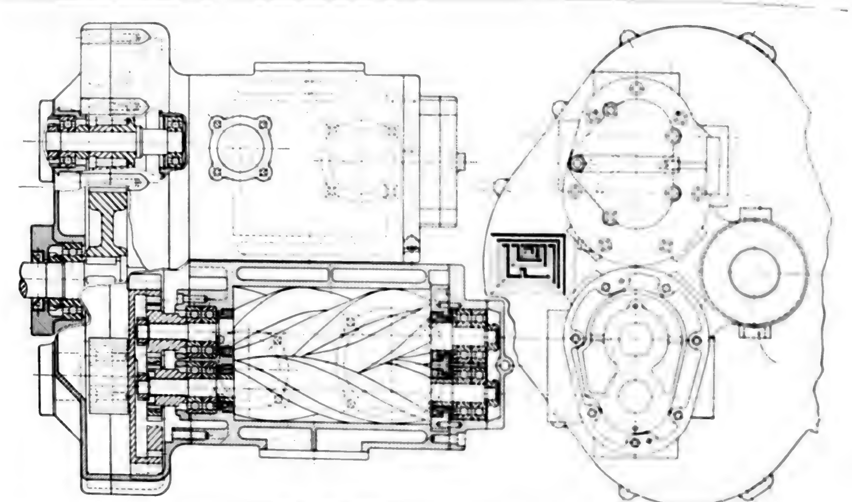


FIGURE 9. Two hundred-cfm Lysholm compressor

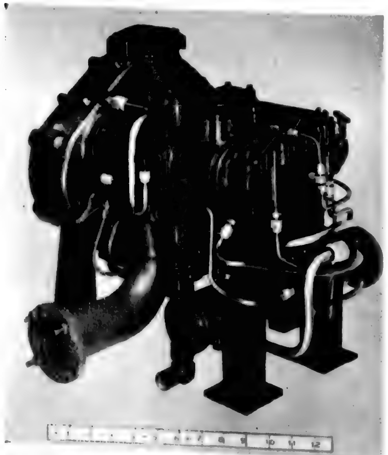


FIGURE 10. Lysholm compressor—weight 165 lb, 180 to 200 scfm at 90 psi.

countershafts through a bullgear-spur pinion combination at 2,590 rpm and 5,180 rpm. Identical internal gears on the countershafts mesh with the male

FIGURE 11. Lysholm compressor rotors.

timing gears to produce the 10,000 and 20,000 rpm speeds.

The inlet and discharge ports are all essentially radial.

Each compressor stage has a cooling jacket which is supplied with oil at 10 psi pressure from an oil pump built onto the gear case. This same oil pump supplies oil to wicks and drip feed for bearings and to spray jets for lubrication of the ground gears. The bottom of the gear case is utilized as a sump for the oil system. The oil is circulated through a filter and an oil cooler (water supplied), both incorporated in the complete unit.

Ball bearings were used throughout the machine. Angular contact bearings were used to take the thrust in the compressor stages and to locate the rotors axially. The bearing life was designed to be 50,000 hr.

The total weight of the unit, as assembled at the end of the testing period, was 165 lb[20] (excluding the intercooler). See Figure 10.

The testing program as originally intended was directed mainly toward the testing of thermodynamic performance and mechanical endurance of the machine, but due to the multitude of mechanical difficulties encountered, it soon took the form of redesign in part, or improvement of the original design.

During the testing period several performance tests were run on each individual stage, and on the unit as a whole. Figures 12, 13, 14, 15, 16, and 17 give performance curves for each individual stage and for the complete unit.

The best data indicate the following performance for operation at the design conditions.

182 cfm of dry air, at 14.7 psia and 60 F (minus approximately 10 cfm for leakage through the seals)
Moisture content assumed to be such that there is saturation at 14.7 psia and 90 F
Shaft input: 54.8 hp at 2,000 rpm
Adiabatic efficiency: 64.7%
Inlet air, 1st stage: 14.7 psia and 120 F
Inlet air, 2nd stage: 120 F
Discharge air: 104.7 psia

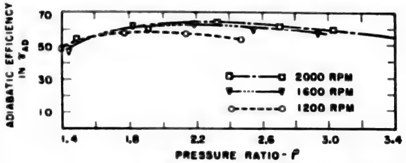


FIGURE 12. Two hundred-cfm Elliott Lysholm compressor—low-pressure stage adiabatic efficiency test.

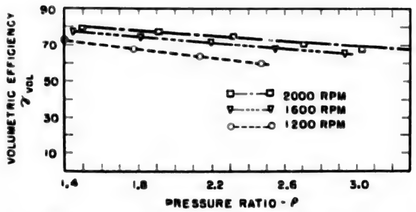


FIGURE 13. Two hundred-cfm Elliott Lysholm compressor—low-pressure stage volumetric efficiency test.

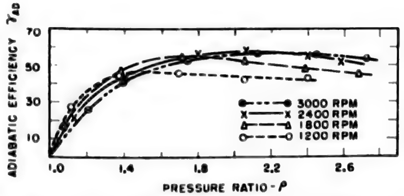


FIGURE 14. Two hundred-cfm Elliott Lysholm compressor—high-pressure stage adiabatic efficiency test.

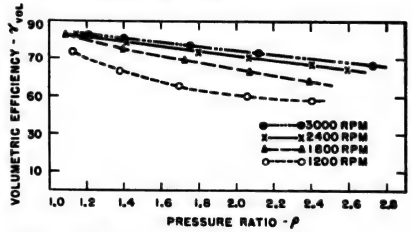


FIGURE 15. Two hundred-cfm Elliott Lysholm compressor—high-pressure stage volumetric efficiency test.

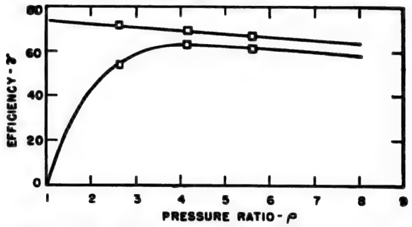


FIGURE 16. Two hundred-cfm Elliott Lysholm compressor unit; volumetric and adiabatic efficiency speed vs pressure ratio, 2,000 rpm.

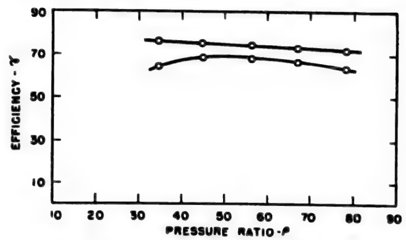


FIGURE 17. Two hundred-cfm Elliott Lysholm compressor—complete unit; volumetric and adiabatic efficiency based on theoretical displacement of low-pressure stage.

To bring the output up to the required 200 cfm of air, the speed would have to be increased from 2,000 rpm to approximately 2,300 rpm.

The maximum operating condition tested for the complete unit is as follows.

211 cfm of gas mixture (minus approx. 10 cfm for leakage through seals)
Shaft speed: 2,000 rpm
Hp input: 59 hp
Adiabatic efficiency: 63%
Inlet air: 13.3 psia, 80 F
Discharge air: 103 psia, 380 F
Pressure ratio: 7.75
Intercooling to: 80 F

The complete unit gave a peak adiabatic efficiency of 68% at a pressure ratio of 5.

The adiabatic efficiency quoted is based on one-stage adiabatic compression from 13.3 to 103 psia.

At the maximum operating condition quoted above the low-pressure stage operates at a 3.3 pressure ratio and the high-pressure stage at 2.4. This checks very closely with the values estimated in the design.

At these pressure ratios the adiabatic efficiencies are 56% and 52% for low- and high-pressure compression respectively (Figures 12 and 14).

The low-pressure compressor has a peak adiabatic efficiency of 64% at 2.3 pressure ratio; and the high-pressure compressor, 56% at 1.9.

The efficiencies given for the separate stages are taken from test runs made with atmospheric inlet conditions for both stages, and only one stage assembled on the gear case at a time. The values given may be somewhat low since in this way more of the gear-case power loss is contributed to each stage than would be the case in the complete unit. The particular tests from which these efficiencies were taken are the best results obtained for each stage.

In an attempt to measure the amount of leakage through the seals in the complete unit, it was found that at least 7 cfm of free air leaked when the unit ran at 2,000 rpm with a discharge pressure of 103 psia.

Any Lysholm compressor is inherently noisy. The *air-noise* is of a rather high pitch (approximately 1,000 and 500 db) due to the high rpm of the rotors. A silencer and filter were used on the inlet, and the discharge was piped to the outside of the laboratory. This reduced the air-noise very considerably. The mechanical noise from the gear case is quite appreciable.

It was decided that much of the remaining air-noise was transmitted through the piping and the intercooler, and an attempt was made to improve the condition by covering all piping with a heavy layer of glass wool. The glass wool lagging cut down the noise from 102 to 95 db as measured with a sound-level meter. (The pick-up was placed at a distance of 8 ft from the compressor.) The noise appeared now to be mainly mechanical, and the noise of the machine was sufficiently low to permit conversation without much difficulty.

To summarize the performance tests, which show that at 2,000 rpm the machine will supply 200 cfm of free air at 103 psia when the inlet air is at 13.3 psia and 80 F, the horsepower input required is 54 with intercooling at 80 F. In the final report on the unit[11] are listed definite proposals for further work on such a compressor suitable for production.

5.5 COMBINATION LOW-PRESSURE AIR COMPRESSOR AND ENGINE DRIVE

To provide the air necessary for operation of the small airborne Collins unit (Chapter 3), it was necessary to develop a lightweight small-capacity compressor to deliver 150 psi air and several extremely lightweight compressors for such service were visualized by contractors for the Army Air Forces, but it was felt desirable to augment such work by a separate development in NDRC. The Clark Company undertook the development of a 30 cfm compressor built integrally with a gasoline engine drive.[16] The unit was referred to as the Bobtail compressor and is so referred to in illustrations and performance curves.

The final design was unique in that it consisted of a 4-cylinder, standard, air-cooled, horizontal-opposed aircraft engine, modified to have two engine power cylinders and two single acting compressor cylinders. Whereas the conventional air compressor has spring-actuated valves, this machine had mechanically operated poppet valves on the first-stage suction. All other valves were spring actuated.

Figure 18 shows the completed assembly, which consisted of the compressor, mounting frame, and Thermek spined-tubing intercooler. Figure 19 is a cross-section drawing showing pertinent details of the compressor cylinders. Table 5 gives the specifications of the unit.

Figures 20, 21, and 22 show the results of performance tests on the compressor which was designed to compress 30 cfm at suction conditions with atmospheric suction and 150 psi discharge pressure.

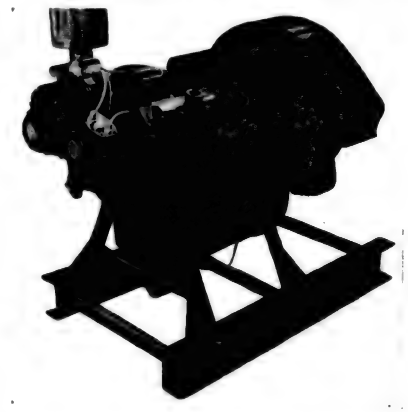


FIGURE 18. Bobtail unit, 31.6 scfm, 150 psi. (2-stage air compressor and engine combined.)

TABLE 5. Specifications Bobtail engine compressor unit.

Type:	Horizontal opposed integral engine
Model:	Bobtail
Compressor data	
Rpm	1,800
Suction pressure	0 psi
Discharge pressure	150 psi
Capacity	30 cfm at intake conditions
Approximate BHP required	15
No. of Cylinders	2
Bore	4 1/4 in. low stage (1) (mech. intake valves)
	4 1/4 in. high stage (1)
Stroke	3 1/2 in.
Engine data	
Rpm	1,800
No. of cylinders	2
Bore	4 1/4 in.
Stroke	3 1/2 in.
Approximate BHP delivered	15.0
Dimensions and weight	
Installation drawing	104-10
Overall length	47 in.
Overall width	30 1/4 in.
Overall height	37 in.
Approximate weight	450 lb.
Accessories supplied	Air-cooled inter-, after-, and oil-cooler, oil pressure and temperature gauges, intake air filters, storage battery, ammeter, and mounting frame

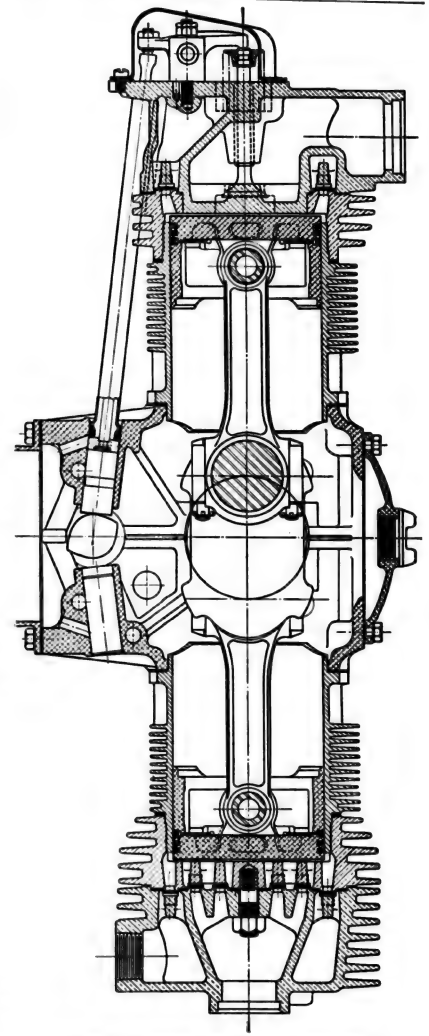


FIGURE 19. Cross-section of Bobtail compressor.

The machine had a number of defects which would render it useless for any commercial purpose. These are: high cost, relatively short life, inadequate oil control, crankcase vapor losses to the compressed air. The unit received thorough testing at Wright Field in connection with the Collins airborne unit.

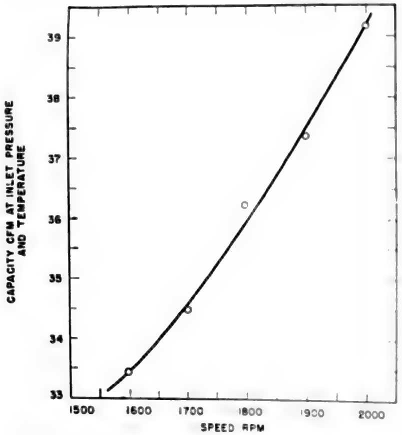


FIGURE 20. Bobtail engine and compressor unit; capacity vs rpm at 150 psi discharge pressure.

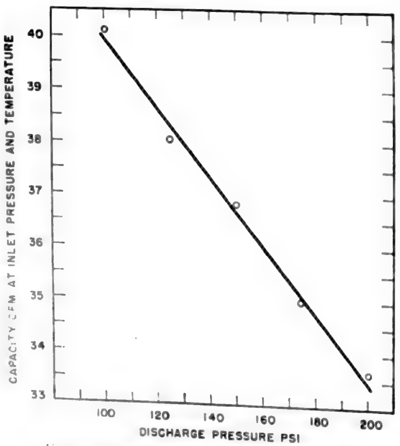


FIGURE 21. Bobtail unit; capacity at 1,800 rpm.

It was not accepted for further development for integration with the Collins unit because it was considered to be quite noisy and was heavier than compressors which the Air Forces felt sure would be developed before the end of the war. The program

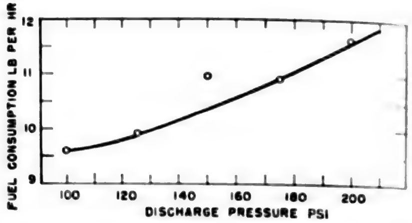


FIGURE 22. Bobtail unit, fuel consumption at 1,800 rpm.

on the Bobtail unit was stopped early in 1943 after delivery of the one model.

5.6 PORTABLE HIGH-PRESSURE COMPRESSORS

Paralleling the development of the low-pressure air compressor, two designs were made up for 3,000-psi lightweight air compressors, especially for the Kellogg M-1 and the Granque unit (see Chapter 4). The first design used for the first two units, although satisfactory, was not considered completely successful; and a second improved design was used in the building of the third and fourth machines of this type.

The first two machines, designated as M-1 compressors, are now obsolete, although the third and fourth, known as the Clark Model H0-6-4 high-pressure portable compressors, have proved to be of use to the Services especially for pressuring air for flame-throwers. At least 85 of these compressors have been supplied for this purpose.

The obsolete design used the Franklin engine crankcase, while the final unit utilizes the more satisfactory Lycoming crankcase, which is also used in the low-pressure compressors previously described.

This high-pressure compressor in its final form is undoubtedly the most successful compressor developed in the NDRC program. Specifications for the unit are given in Table 6. Figure 23 shows the air compressor mounted on a base ready for attachment of an engine or motor drive. Figure 24 shows the compressor fully connected and suitable for operation in flame-thrower work. Figure 25 gives the cross-section of the first-stage cylinder.

Compressor performance is illustrated graphically in Figures 26 and 27. Interstage pressure data at several speeds are also tabulated in Table 7.

TABLE 6. Specifications Clark Model H0-6-4, six cylinder, four stage, horizontal opposed compressor.

Type:	6-cylinder, four-stage, horizontal opposed cross-head, oil lubricated, full force feed		
Model:	H0-6-4		
Stages	*First*		*Second*
No. of cylinders	3		1
Bore	5 in.		4 in.
Stroke	3 7/8 in.		3 7/8 in.
Stages	*Third*		*Fourth*
No. of cylinders	1		1
Bore	2 in.		1 3/16 in.
Shift	3 7/8 in.		3 7/8 in.
RPM		900–1,800	
Suction pressure		0 psi	
Discharge pressure		3,000 psi	
Capacity			
At 900 rpm		63.5 cfm	
At 1,800 rpm		127.0 cfm	
BHP			
At 900 rpm		Approx 40	
At 1,800 rpm		Approx 100	
Dimensional data			
Installation drawing		108–130	Complete with cooler, etc.
Overall height		64 1/8 in.	
Overall length		63 1/4 in.	
Overall width		45 in.	
Weight without cooler and frame		1,000 lb.	
Weight complete with cooler and all accessories		2,150 lb.	
Accessories supplied	Oil pressure and temperature gauges, oil filter, force feed lubricator and interstage manifolds		
Optional equipment	Mounting frame, interstage piping, gauges, air-cooled inter- and after-cooler, knockout traps and over-pressure control		

TABLE 7. Interstage pressures Model H10-6-4 compressor.

	3,000 psi discharge			
	1,900 rpm		750 rpm	
1st stage suction	0		0	
1st stage discharge		52		49.4
2nd stage suction	49.7		48	
2nd stage discharge		180		194
3rd stage suction	178		193	
3rd stage discharge		720		665
4th stage suction	670		630	
4th stage discharge		3,000		3,000
	2,000 psi discharge			
	1,900 rpm		850 rpm	
1st stage suction	0		0	
1st stage discharge		47		46.5
2nd stage suction	44		45	
2nd stage discharge		178		183
3rd stage suction	176		182	
3rd stage discharge		645		600
4th stage suction	600		555	
4th stage discharge		2,000		2,000

All pressures pounds per square inch gauge

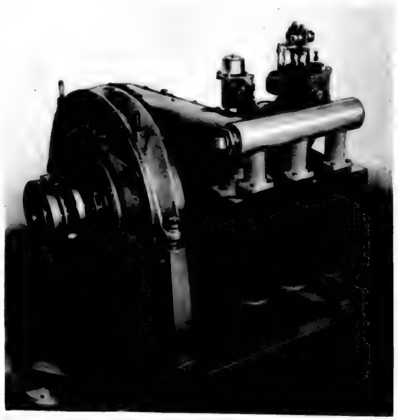


FIGURE 23. Clark 3⅞-in. stroke 6-cylinder, 4-stage 0-3000-psi compressor.

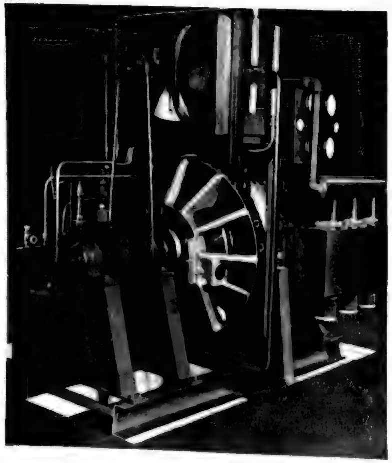


FIGURE 24. Clark compressor and intercooler, 120 scfm, 3,000 psi discharge.

The horsepower data shown in the curves were calculated from electrical readings for power input to the direct-current drive motor. It is believed that the actual horsepower consumption is 92% of that shown on the plots.

5.7 450-HORSEPOWER LOW-PRESSURE AND INTERMEDIATE-PRESSURE AIR COMPRESSORS

In connection with the large-scale liquid oxygen pilot plants, M-5 and M-6[15] (Chapter 3), it was desirable to build compact compressors to supply them with air. For the M-5 plant a compressor was designed to supply 2,160 cfm from 0 psi to delivery at 90 psi. For the M-6 unit where the operation was to be at 600 psi it was thought that a unit could be developed to supply 1,060 cfm at 0 psi for delivery at 612 psi. This latter machine was to have compressor cylinders which could be attached to the low-pressure compressor; thus either of the two desired pressures and capacities could be developed from the same basic design. The compressor that was built was a 6-cylinder, 12-in. stroke, 600-rpm unit which could mount either five 10-in. bore x 12-in. stroke, double-acting, low-stage cylinders and one 10 x 12-in. double-acting, high-stage cylinder for the 0 to 90-psi condition or 10, 10, and 5 x 12-in. first-, second-, and third-stage cylinders for the 0 to 612-psi condition. It was planned that all tests requiring the 90-psi air would be completed and then the 612-psi cylinders would be mounted for the balance of the tests.[11]

The compressor unit was completed in the summer of 1943 and was shipped to the Central Engineering Laboratory at Philadelphia, before any tests were made on the 612-psi cylinders. The machine has not been run with these high pressure cylinders although the cylinders are at hand.

Figures 28 and 29 are pictures of the compressor installed in the laboratory at Philadelphia, directly connected to a Clark 10 x 12-in., 8-cylinder, vertical diesel supplied by the U.S. Navy. Table 8 gives the specifications for the compressor. Charts showing performance as checked during the brief tests at Olean, N.Y., are shown in Figures 30, 31, and 32. Other performance data can be obtained from the operating records of the M-5 unit[14] (see Chapter 3).

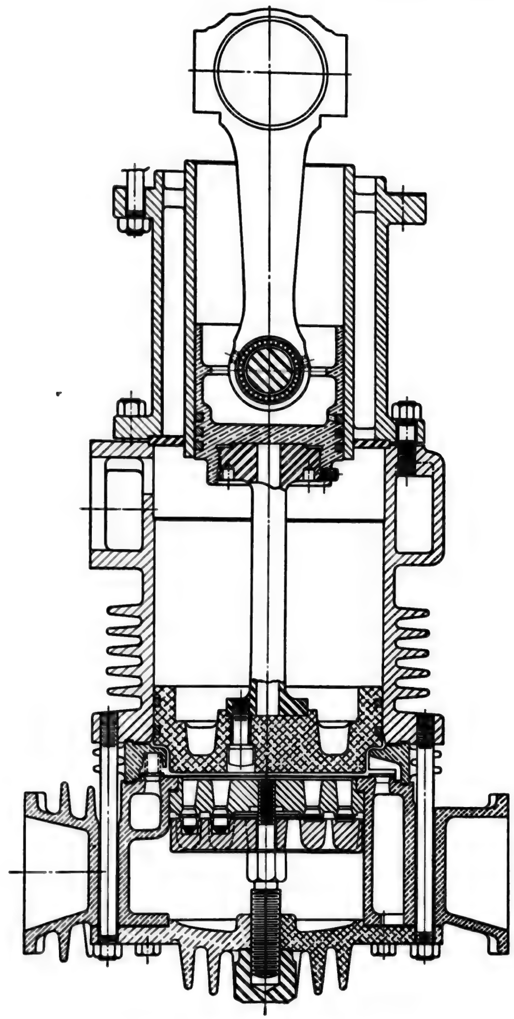


FIGURE 25. Cross-section of first-stage cylinder in final design 3⅞-in. stroke four stage compressor

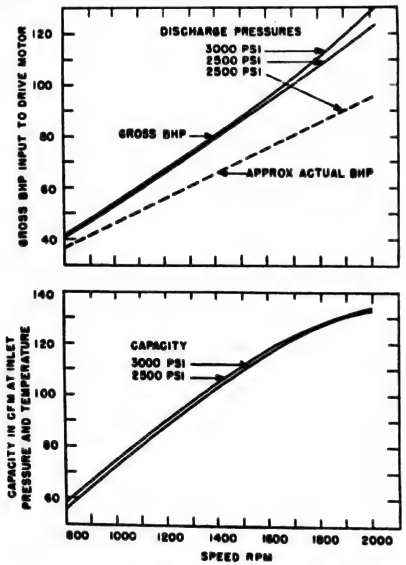


FIGURE 26. High-pressure compressor power capacity and speed data.

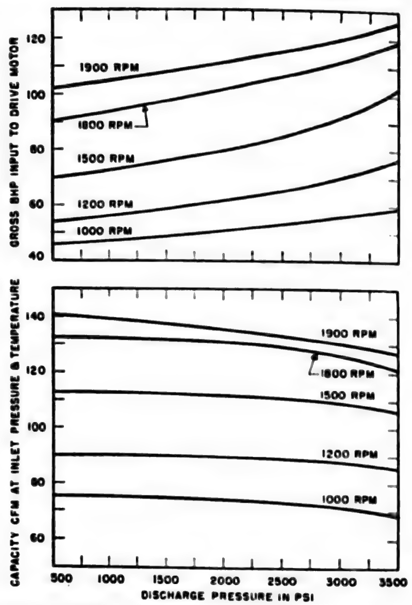


FIGURE 27. High-pressure compressor capacity performance data.

TABLE 8. Specifications Clark 10 in. x 12 in. vertical, 450-hp air compressor.

Type: Vertical, 6-cylinder, double-acting air compressor arranged for direct connection to engine	
Model: CVC-12	
Compressor data	
Gas to be compressed	Air
Capacity	2,100 cfm at intake conditions
Suction pressure	0 psi
Discharge pressure	90 psi
RPM	600
BHP required (approx)	525
No. of cylinders (compressor)	6
Type	Double acting
Bore	10 in.
Stroke	12 in.
Arrangement	5 low stage 1 high stage
Dimensions and weight	
Installation drawing	91465
Overall length	12 ft 4 ⅛ in.
Overall width	3 ft 10 in.
Overall height	8 ft 3 ¾ in.
Total weight	25,000 lb
Accessories supplied	Oil pump, oil pressure and temperature gauges, full force-feed lubrication and half flywheel coupling

5.8

EXPANSION ENGINES

One of the necessary features for successful adaptation of a low-pressure cycle for the liquefaction of air and its subsequent fractionation is a highly efficient expansion engine. S. C. Collins built and perfected a small reciprocating expansion engine[24,25] which offered great promise for use not only in the very small airborne oxygen plants but also for the portable 1,000 cfh producers. Further work was done to develop the original Collins expander in the small size necessary for the Collins unit and also the Clark Company developed several larger size reciprocating expanders based essentially upon the Collins expander.[11]

5.9

COLLINS SMALL-SIZED RECIPROCATING EXPANDER

The reciprocating expansion engine is a closely fitting piston and cylinder equipped with intake and exhaust valves much the same as a steam engine.

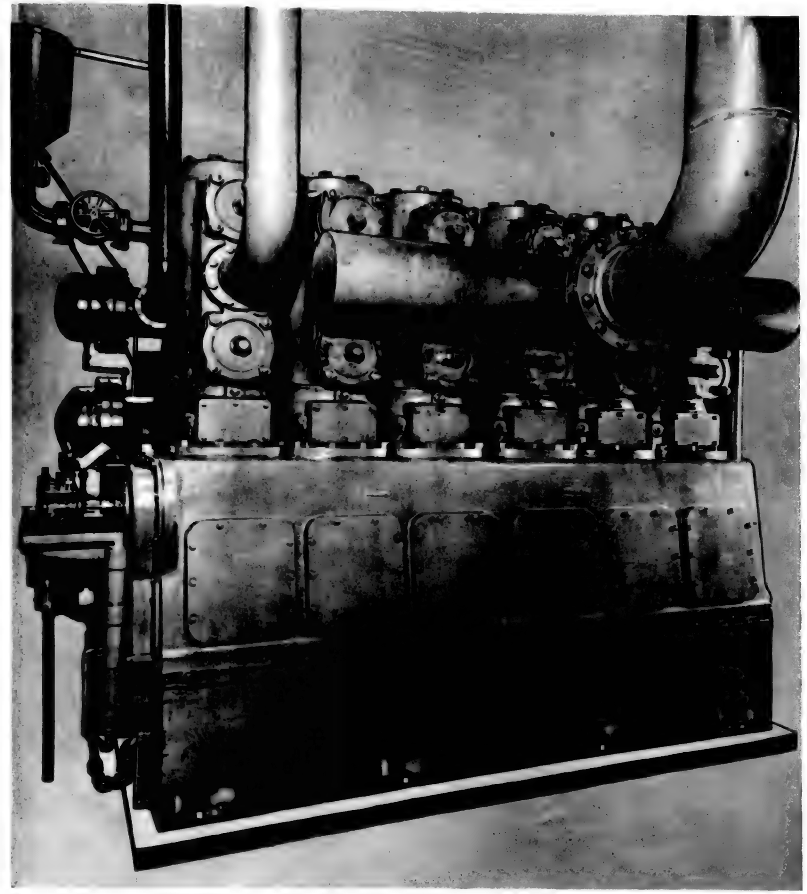


FIGURE 28. Installation view Clark two-stage vertical M-5 compressor at NDRC Philadelphia Laboratory.

The general arrangement is illustrated in the sketch of Figure 33. The piston has a diameter of 2 in. and a stroke of 2 in., making a displacement of 6.28 cu in. The most suitable difference in diameter between piston and cylinder has been found to be 0.0008 to 0.001 in. Experiment over a range of clearances from 0.0002 to 0.0015 in. have shown that if the fit is better than a half-thousandth of an inch there is a great danger of severe friction developing because of small particles of solid carbon dioxide or other solid impurities. If the fit is poorer than one-thousandth of an inch an excessive amount of air leaks by the

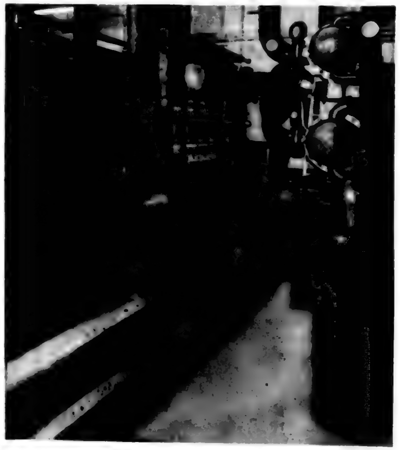


Figure 29. Diesel engine and compressor.

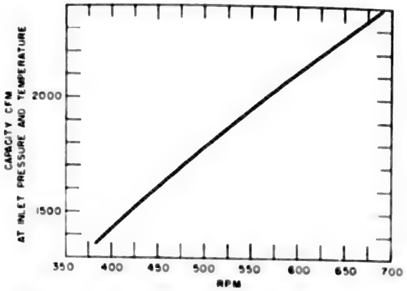


Figure 31. Six-cylinder vertical 12-in. stroke compressor—capacity at 90 psi.

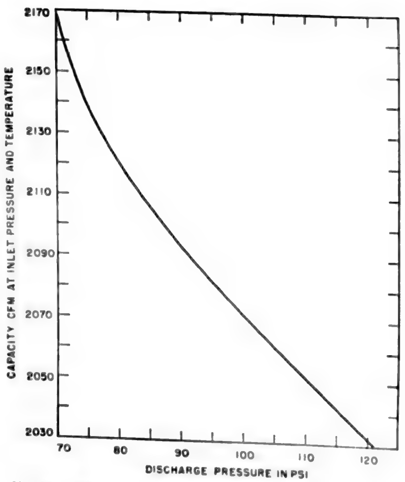


Figure 30. Six-cylinder vertical 12-in. stroke compressor—capacity at 600 rpm.

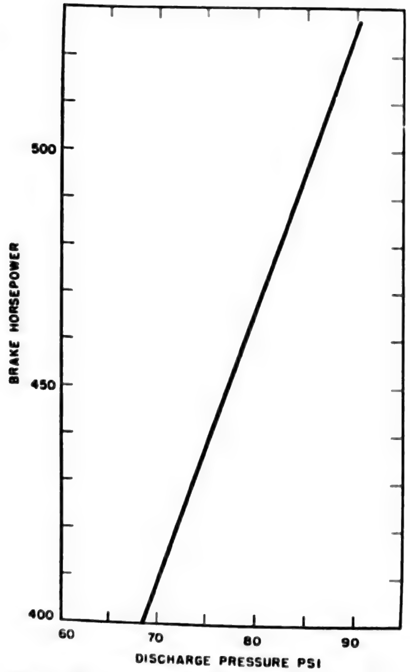


Figure 32. Six-cylinder vertical 12-in. stroke compressor—horsepower at 1,600 rpm.

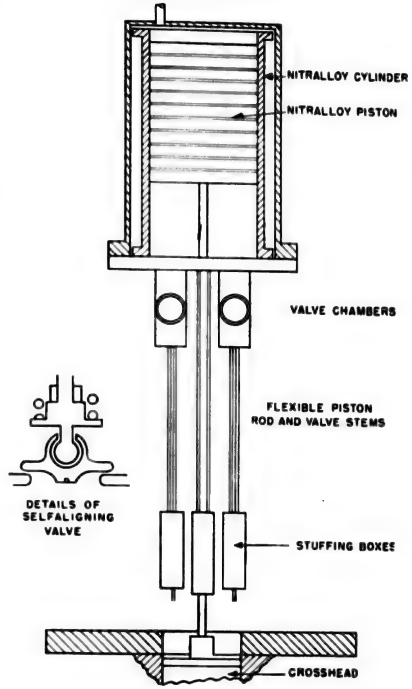


Figure 33. Expansion engine cylinder.

piston and the efficiency of the engine is reduced correspondingly.

The piston and cylinder are made from nitralloy steel and are hardened, ground and polished to resist wear (Figure 34). There is no lubrication other than the thin film of air. If the proper clearance is allowed there is never any trouble from seizure and the leakage of air is about 1%. No trouble has yet been encountered from rust, although it is conceivable that if the machine is allowed to stand idle for some months while wet, a mild seizure may result. No trace of wear has ever been detected on any piston or cylinder even after 2,000 hr of operation.

During operation the piston and cylinder are at approximately the temperature of liquid air and must therefore be insulated in order to conserve refrigeration. For this reason a thin-walled stainless steel cylinder and long piston rod and valve stems are used to isolate the expansion cylinder from the crosshead and crankcase, and at the same time to offer sturdy mechanical support. The piston rod is a ¼-in. diameter stainless steel rod fastened to the nitralloy piston at the upper end and to the aluminum crosshead at the lower end (Figure 35).

Figure 34. Expander parts.

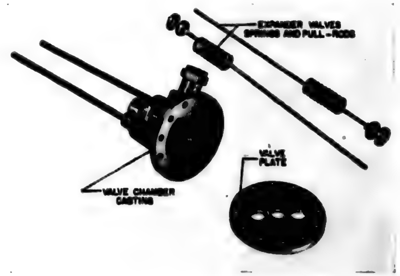


Figure 35. Expander parts.

The rod is not fastened rigidly to the nitralloy piston because of the possible lateral stress which it might exert due to slight misalignment. The coupling is similar to a ball-and-socket joint except that only a very slight deflection need be allowed for, and it is important to have no longitudinal play. A closely fitting stainless steel tube is used to house the piston rod, and a stuffing box at the end of this tube in the warm region serves to prevent leakage from the expansion cylinder. The tube must be closely fitting

because the annulus between tube and rod forms part of the dead space in the expansion cylinder; and this must be kept to a minimum for high efficiency.

The expander valves are actuated by cams located on the crankshaft on which rollers ride attached to rocker arms. The motion is transmitted from the rocker arms to the valves by thin stainless steel pull rods running through the crosshead, through stuffing boxes, and up through stainless steel housing tubes. Because of the total lack of lubrication the valves cannot be accurately guided, and must therefore have self-aligning features to enable them to sit squarely on their seats. Each valve is coupled to its pull-rod by a ball-and-socket type of union which is free to align itself. The valves are held against their seats by strong stainless steel springs, too strong to be overcome by the maximum pressure developed in the expansion cylinder, but not too strong to be opened by the pull-rod and cam mechanism.

The valve chamber is an aluminum casting having a partition which separates it into two compartments. The exhaust valve is in one compartment and the intake in the other (Figure 35). Each compartment receives a bronze pipe fitting to which is soldered a copper tube carrying the intake and exhaust air. Thin annealed aluminum gaskets are used to secure a pressure-tight seal between the valve chamber and valve plate, also between the valve plate and expander cylinder, and again between the cylinder head and cylinder. The cylinder head which bolts on top of the assembly is fitted with a ¾-in. pipe connection to the exhaust surge chamber. This enables the region back of the nitralloy piston to breathe and also recovers any air leaking past the piston.

The valve timing in the engine is as follows: the intake valve opens 5 degrees before bottom center and closes 51 degrees before top center; the exhaust valve opens 10 degrees before top center and closes 10 degrees before bottom center. The valve lift is $\frac{3}{16}$ in.

The efficiency of the expander operating at liquid air temperature has not been appraised accurately because of the difficulties involved in estimating insulation heat leaks and various other factors with any accuracy. The most careful estimates indicate efficiencies of 80% or better.[37]

The crankcase assembly is fairly standard in design. The crosshead, connecting rod and crankcase itself are machined from aluminum castings. The crank, wrist pin, rocker arms and crosshead cylinder liner are steel. One unique feature is the fact that the cams are an integral part of the crankshaft and the valve pull rods pass through holes in the reciprocating crosshead.

Several attempts, with little success, were made to find a satisfactory substitute for the nitralloy piston and cylinder combination, not because of any malfunction of the device, but simply because of the precision machining and grinding and expensive heat treatment required.[11]

Various materials were tried out as packings in the piston rod and valve rod stuffing boxes. Some of these were artificial rubber (several types), multiple rings of thick hard leather, multiple rings of thin flexible leather, moldings of graphitized asbestos, and standard graphitized asbestos rope. The most durable combination was found to be graphitized asbestos (either molded or in rope form) confined between leather follower rings. Oil-resistant neoprene is satisfactory for the valve rod stuffing boxes where the amount of motion is small.

5.10 CLARK-COLLINS EXPANSION ENGINES

5.10.1 Two-Cylinder 4 x 3½-in. Engine

The small Collins expansion engine was a single-cylinder unit whose principle features were that pistons were without rings; the piston rods were flexible and of small diameter; the valves were flat seat, non-guided; packing glands operated at room temperature; and stainless steel was used to cut heat leak.[11] In laying out the design for a 2-cylinder machine for twice the capacity of a single-cylinder Collins unit, the same features were retained and in addition there was built into the machine a loading device to dissipate the mechanical work of expansion, and a crankshaft and valve gear. Figure 36 gives a cross-sectional view of the final unit as used in the production models. Figure 37 is a picture of the machine. Table 9 gives the specifications for the unit. Detailed information on the development of the expander is covered in various progress reports.[4,7,13,14] The performance of the expander can be illustrated by Figures 38 through 41. These curves illustrate but a few of the characteristics and are given here to show those of prime interest. Figure 38 illustrates the motion as controlled by a steel cam. Figure 39 illustrates speed-efficiency relations for several discharge pressures, Figure 40 shows the speed flow relations at the same

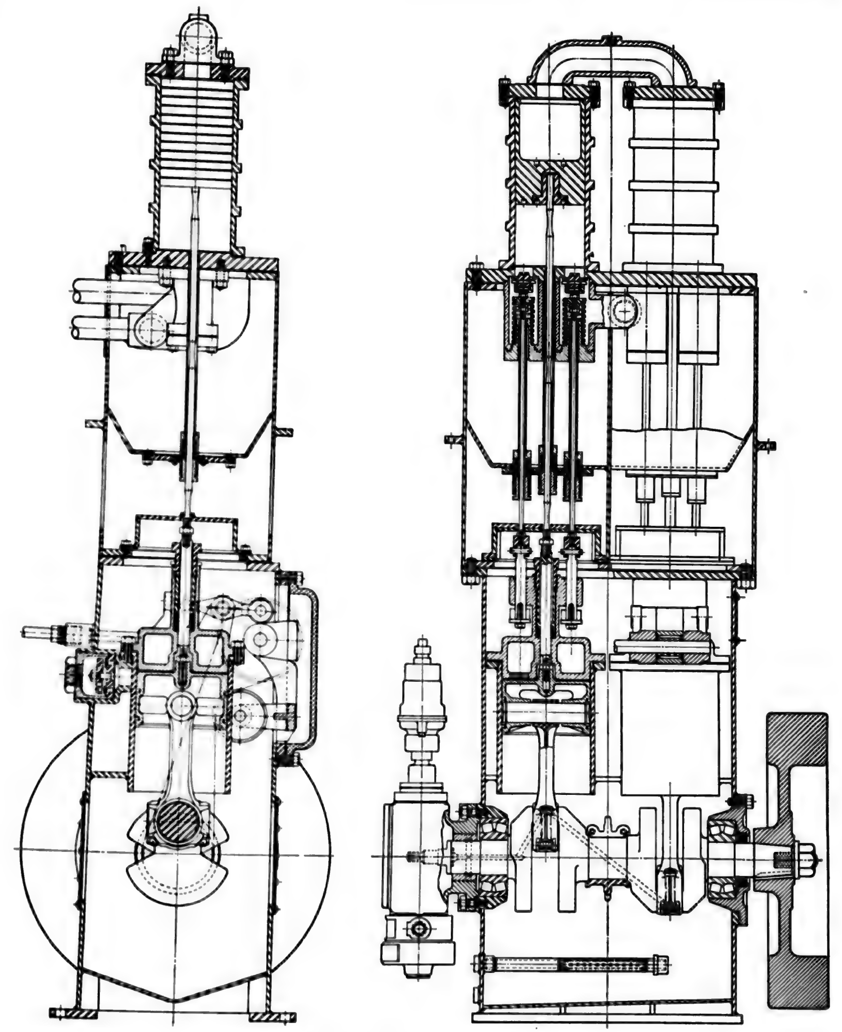


Figure 36. Cross-section of final Clark-Collins expander

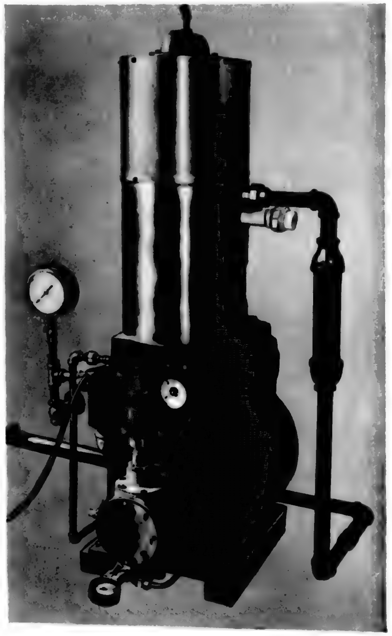


FIGURE 37. Expansion engine, 290 lb air/hr, air-film lubricated, 86 psi to 6 psi.

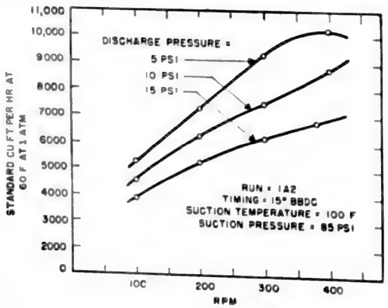


FIGURE 38. Reciprocating expander characteristics.

TABLE 9. Specifications Clark-Collins Model CCER-3 two cylinder expansion engine.

Type: Collins vertical 2 cylinder crank end expansion integral compressor	
Model: CCER-3	
Expansion end specifications:	
No. of cylinders	2
Bore	4 in
Stroke	3 [illegible] in
Cylinder type	Lap fitted piston and cylinder ringless piston
Compressor end specifications:	
No. of cylinders	2
Bore	4.5 in
Stroke	3 [illegible] in
Cylinder type	Conventional trunk type piston, 1 compression and 1 oil control ring
Design operation conditions:	
Design inlet pressure	100 psia
Design exhaust press	22 psia
Design inlet temp	250 F
Design exhaust temp	306 F
Capacity	250 lb per hr
RPM - design	300
Material specifications:	
Main lower crankcase	Welded steel
Upper crankcase	Welded stainless steel
Lower cylinder head	Stainless steel plate
Exp. air manifold	Bronze casting
Exp. cylinder	Nitralloy H - nitrided - hone finish
Exp. pistons	Nitralloy H - nitrided - hone finish
Valves	Stainless steel
Valve springs	Stainless steel
Piston rods	Stainless steel
Valve pull rod	Stainless steel
Packing exp. end	Dry asbestos
Air comp cyl	Steel weldment
Air comp piston	Bronze casting - cast iron rings
Dimensional data	
Installation drawing	102-104
Overall height	57 1/16 in.
Overall width	17 in.
Overall length	24 13/16 in.
Weight, complete unit	650 lb (including insulation)
Accessories supplied	Oil pump, gauge and special wrenches

discharge pressures. Figure 41 illustrates the effect of speed and discharge pressure on the refrigeration obtainable.

At least 50 production models of this expander have been built and they have been found to be very dependable, easily serviced and, in general, have met the requirements of the Services with regard to lightness in weight and compactness combined with high efficiency. In continuous use, expansion efficiencies of a little more than 60% are being realized. With ordinary maintenance several of these machines have run for over three thousand hours.

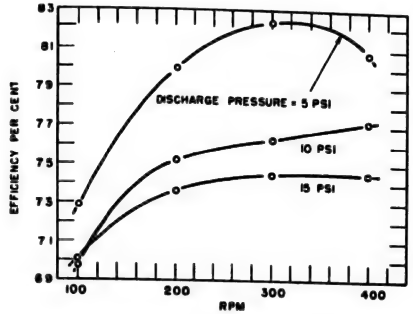


FIGURE 39. Reciprocating expander characteristics.

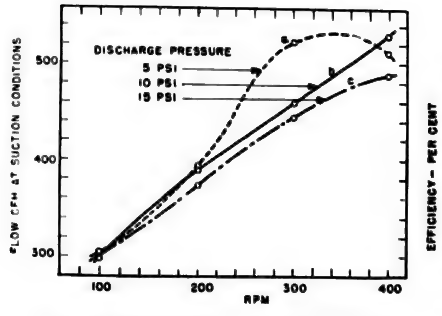


FIGURE 40. Reciprocating expander characteristics.

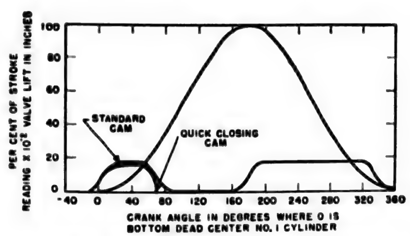


FIGURE 41. Reciprocating expander characteristics.

5.10.2 Two-Cylinder 3x2-in. Walking Beam Type Engine

After the highly successful operation of the 2-cylinder expansion engine just described, it was felt desirable to build an engine for capacity of 150 lb of air per hr or approximately one-half the capacity of the larger engine and to operate between pressures of 100 psia and 22 psia.[11] This expander was to fit the requirements of an intermediate capacity low-pressure oxygen unit described in Chapter 3 under the heading of Medium-Capacity Air Transportable Unit—the M-3.[15]

In order to obtain the most compact 2-cylinder unit, it was desirable to change the larger design from the straight line arrangement of the original Collins unit and a so-called walking beam mechanism was developed. When this motion was combined with a small gear-driven flywheel, a combination crankshaft and camshaft, and a combination lubricating oil pump and loading brake utilizing the flywheel gearing, resulted in a 2-cylinder engine weighing less than 130 lb. Figure 42, a cross-sectional view of this machine, shows the ingenious arrangement which resulted in this lightweight unit.

This type expansion engine, while utilizing several new mechanical modifications, did not dispense with the time-tried Collins features noted in the previous section. Comparison with the cross-sectional view in Figure 36 shows the similarity between the machines.

One machine was built up with valve equipment arranged for 80% cut-off as against the original design of 25%. The crankshaft was extended so that the work could be absorbed by means of a gear-driven motor generator rather than the lube oil pump; this to facilitate operation at constant speed as required by the Collins cycle. (See Chapter 3.)

Reports from Philadelphia[27] and Cambridge tests[11] indicate that the thermal efficiency was about 70% under normal operating conditions. Table 10 gives the specifications of the unit.

No commercial use has been made of the walking beam expander. The M-3 oxygen producing unit does not fit Service needs and further development of the expander was not carried out.

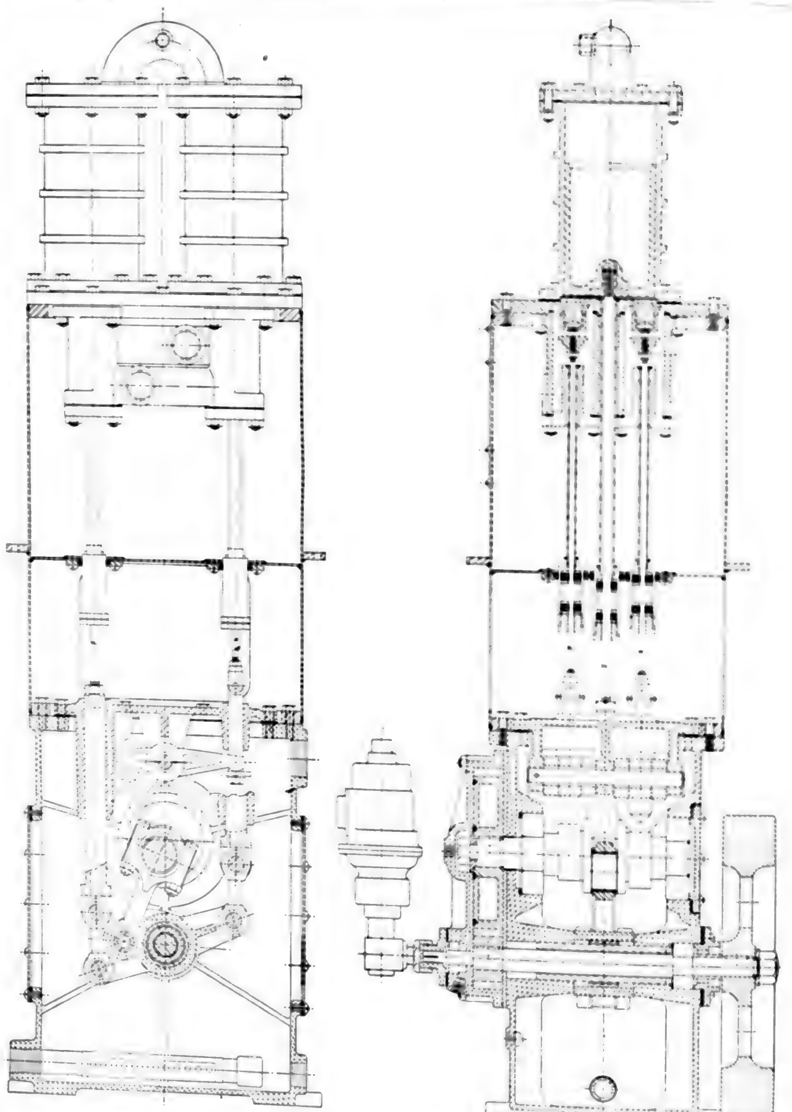


FIGURE 42. Cross-section of Clark-Collins walking beam expander.

TABLE 10. Specifications Clark-Collins walking beam two-cylinder expansion engine.

Type: Collins vertical 2-cylinder, crank-end expansion, walking beam, oil pump loading device.	
Model: WBEx-1	
Expansion end specifications	
No. of cylinders	2 in.
Bore	3 in.
Stroke	2 in.
Cylinder type	Lap-fitted ringless piston and cylinder
Material specifications	
Main lower crankcase	Cast aluminum
Upper crankcase	Welded stainless steel
Lower cylinder head	Stainless steel plate
Exp air manifold	Bronze casting
Exp cylinder	Nitralloy H - nitrided - hone finish
Exp pistons	Nitralloy H - nitrided - hone finish
Valves	Stainless steel
Valve springs	Stainless steel
Piston rod	Stainless steel
Valve pull rod	Stainless steel
Packing exp. end.	Dry asbestos
Design operating conditions	
Design inlet pressure	100 psia
Design exhaust pressure	22 psia
Design inlet temp	-250 F
Design exhaust temp	-306 F
Capacity lb/hr	150
Flywheel rpm	900
Cylinder strokes per min per cyl	300
Dimensional data	
Installation drawing	110-01
Overall height	37¼ in.
Overall width	11⅛ in.
Overall length	15⅛ in.
Overall weight	125 lb
Accessories supplied	Oil piping and oil gauge

TABLE 11. Specifications Clark two-cylinder, vertical, high-pressure expansion engine.

Type: Vertical, 2-cylinder, head-end expansion, external loading device.	
Model: HLE-1	
Expansion end specifications	
No. of cylinders	2 single acting
Bore	4½ in.
Stroke	7 in.
Cylinder type	Long plunger-type piston—ringless, in lap-fitted cylinder
Design operating conditions	
Design inlet pressure	600 psia
Design exhaust pressure	74 psia
Design inlet temp	−130 F
Design exhaust temp	−260 F
Capacity	3,383 lb per hr
RPM design	300
Material specifications	
Main lower crankcase	Welded steel
Upper crankcase	Welded stainless steels (18–8)
Upper cylinder head	Bronze casting
Intake manifold	Bronze casting
Exhaust manifold	Bronze casting
Expander cylinder	18–8 stainless and nitralloy lower
Expander pistons	18–8 stainless and cast iron lower
Valves	Invar steel
Valve stems	Invar steel
Dimensional data	
Installation drawing	109–37
Overall height	79 $\frac{1}{16}$ in.
Overall width	24½ in.
Overall length	39 in.
Approximate weight	1,200 lb
Accessories supplied	Oil pump, oil gauge, V belts, "Hydrotarder" loading brake, and water cooler

5.10.3 Two-Cylinder 4½x7-in. High-Pressure Expansion Engine

For the M-6 liquid oxygen pilot (see Chapter 3), a high-pressure expansion engine was developed.[11] In most particulars the same general principles and construction used for the previously described reciprocating expanders were used. Specifications for the unit are shown in Table 11. A cross-sectional drawing is shown in Figure 43.

The design consists of a conventional crankshaft, connecting rod, and crosshead but the upper or expansion end is rather unusual. The expansion end crankcase is fabricated from 18-8 stainless steel as in the other expansion engines but the expansion takes place on the head end rather than on the crank end of the cylinders as in the other expansion engines. The valves are mounted in the head and a long piston operating in an extremely long cylinder without piston rings enables this machine to operate efficiently and with an extremely low amount of air and heat leakage. The valves and valve guides are unusual in that no packing is utilized. A seal is maintained merely by close tolerances.

Whereas the other units have had a built-in loading brake, the Clark high-level expansion engine is V-belt connected to a Parkersburg Rig & Reel Co. "Hydrotarder," a novel form of hydraulic dynamometer. This arrangement gives the same type of variable speed operation as is found on the smaller Clark-Collins' expansion engine.

Tests of the high-level expander operating in the M-6 plant, made at Stamford and totaling about 300 hr indicate that the engine is capable of expanding air with a heat drop efficiency of 85% under the conditions of operation required.[15,38] Mechanical operation

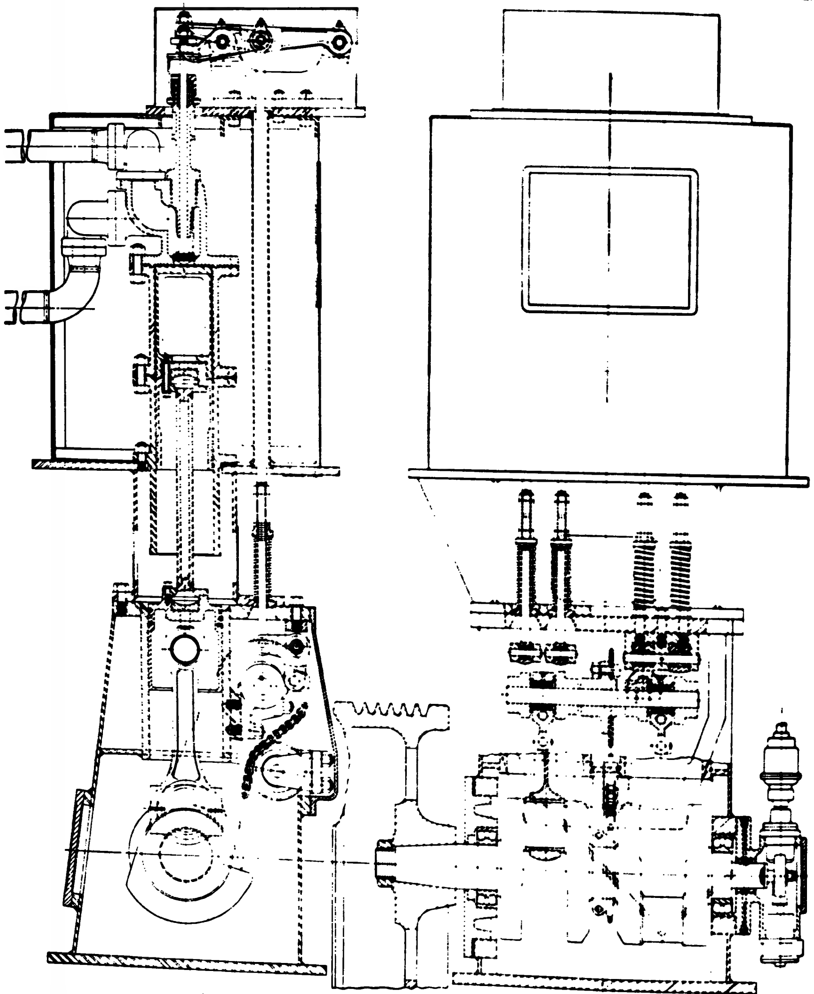


FIGURE 43. Cross-section of Clark high-pressure expander.

has been entirely satisfactory at speeds up to 275 rpm but it is not considered practical to operate at speeds over 300 rpm. Owing to this speed limitation it has been necessary to increase the cut-off to about 32% in order to get sufficient throughput to run the M-6 unit at designed conditions and at this increased cut-off the efficiency has dropped to about 80% because of incomplete expansion.

5.11 TURBINE-TYPE EXPANSION ENGINES

5.11.1 Large Turbo-Expander, Capacity 7,050 Lb of Air Per Hr

One of the important mechanisms required to achieve compact design for low-pressure air liquefaction is an efficient expansion engine. Kapitza in Russia was reported to have had success in the operation of a turbine type expander, and it was rumored that the Linde Company in Germany had used such an expander in connection with Linde-Fränkl oxygen units. No data were available in this country on the design or performance of such expanders and one of the first projects laid out by this section was that of producing a high-capacity turbo-expander. The unit was projected as a part of the M-5 unit (see Chapter 3), and indeed it was necessary to set up the M-5 plant before the turbo expander could be tested thoroughly under the required pressure and low-temperature conditions.

The quantity of air necessary to expand in order to obtain a given amount of refrigeration is inversely proportional to the efficiency of the expander; thus high efficiency is essential to the success of the application. The quantities involved, especially in this particular job, would be large for a reciprocating machine but are quite small as turbine sizes go. Conventional turbine seals were too imperfect and a special shaft seal had to be worked out; because of the low temperature a selection of materials was limited; cold losses to the surrounding atmosphere constituted another difficulty; and the high speed at which the machine needed to operate introduced a critical shaft problem and a bearing problem. Because of their inter-relation, the problems had to be studied more or less simultaneously, but they are presented separately below.

It was concluded at the outset that the turbine would have to be of simple design and that it would have to be either a single-stage axial impulse turbine or a radial turbine. A preliminary design of the axial turbine revealed wheel construction difficulties, a difficult critical shaft problem because of a heavy turbine wheel, probable low nozzle efficiency, and an insufficiently high overall efficiency estimated at 71%.[19,20,22,[illegible]]

An investigation of the radial turbine showed that the turbine wheel would be lighter and easier to construct and should have substantially higher efficiency if properly proportioned. Accurate and complete data on the impulse-type turbine were available so that its characteristics were rather easily estimated, but very little was known about the radial turbine, and almost every phase of it had to be rather carefully studied.

FINAL DESIGN

The final arrangement of the turbine,[26,34] shown in Figure 44 consisted of a 6⅞-in. OD aluminum turbine wheel mounted on a 1-in. shaft in cantilever fashion 3 in. from the nearest bearing. The shaft was supported in two bearings. The one nearest the turbine was a sleeve bearing and it also constituted the shaft seal. The bearing farthest from the turbine wheel carried the thrust load and it was a ball bearing. This bearing assembly was supported upon the turbine case by means of a thin walled stainless steel sleeve of rather large diameter. Thus mechanical strength was attained without undue cold loss from the cold turbine case. The shaft between the warm bearing and the cold turbine wheel, being 3 in. long and of stainless steel, resulted in a negligible heat leak.

The case was a stainless steel casting in two parts. The nozzles were built into a separate assembly which fit in between these two parts. The turbine was mounted by the case by means of three 3-in. diameter stainless steel tubes 6 in. long so arranged that temperature changes would not disturb the shaft alignment between the turbine and the loading device to which it was coupled. The length of these tubes was sufficient to extend through the insulation and to prevent any but negligible loss by conduction. Measurement of shaft mis-alignment as a result of various loads applied to the suction and discharge flanges, showed that this means of support was adequate, if suitable expansion joints in the connections were used.

Operation. The operation of the turbine is as follows. The cold high-pressure air (103 psia and −242 F) enters the volute chamber and passes through the peripheral nozzles by which the air is accelerated in a tangential direction to a little over 600 ft per sec and in a radial direction to about 100 ft per sec. At this point, it enters the periphery of the wheel. The wheel has radial blades and the periphery of the wheel is traveling at a little over 600 ft per sec so there is no shock at this point. The gas flows inward between the radial blades and is uniformly decelerated to about 300 ft per sec before it

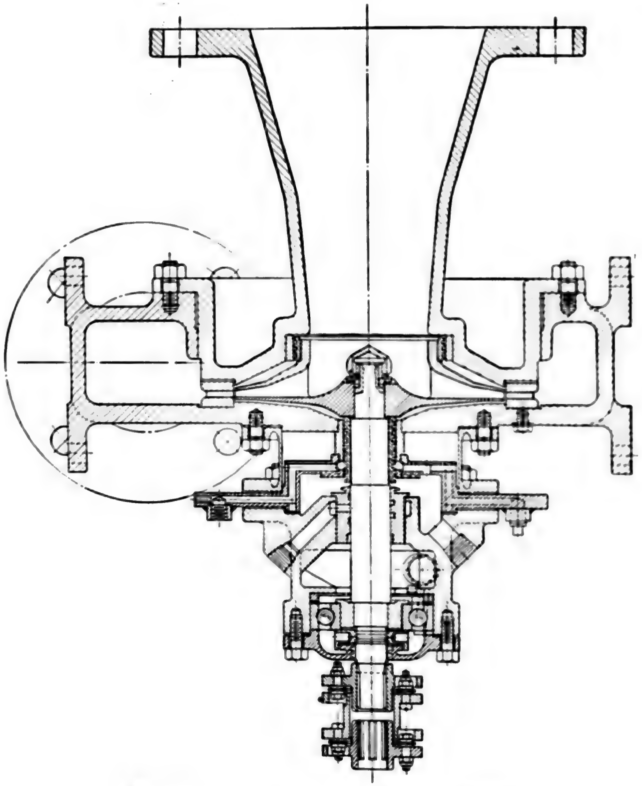


FIGURE 44. Assembly drawing of large turbo expander.

reaches the wheel discharge at 20 psia. At the wheel discharge the blades are so curved as to form another set of nozzles which are directed backward with relation to the direction of wheel rotation, and the gas is discharged from these nozzles at a relative velocity of about 300 ft per sec. Thus the air is discharged from the wheel with no rotational velocity. It works out that about half the energy in the air is spent in the primary nozzles, about 35% is spent in opposing the centrifugal force field within the wheel and about 15% in the wheel discharge nozzles. The efficiencies at which these various transformations of energy were accomplished were either measured in special apparatus or estimated, and on the basis of these figures the turbine elements were so proportioned as to minimize the total losses.[34]

During operation, the prevailing pressure around the shaft is 25 or 30 psi. The leak rate of conventional seals would permit a prohibitive loss of cold air, so the inboard bearing was made a sleeve bearing and was used at the seal. Oil was delivered to this bearing under sufficient pressure that a portion of it flowed each way axially along the bearing clearance. The portion which flowed inwardly flowed into a

chamber which communicated directly with the pressure around the shaft. An adequate system of baffles was arranged around the shaft so that the oil did not enter the air stream. The oil drained into a chamber whence it was automatically trapped to the atmospheric storage reservoir. The portion of the oil which flowed outward passed over a weir and its level was thus maintained at such a point as was necessary to lubricate the ball bearing properly.

Loading Device

The turbine was direct-coupled by means of a special Thomas flexible coupling to a reducing gear wherein the speed was reduced from 22,000 rpm to 3,600 rpm. The 3,600 rpm shaft was direct-coupled by means of another Thomas coupling to an Elliott 35 kw, 110 v, d-c generator. The power generated by the turbine was thus converted to electrical energy and spent in a suitable Westinghouse resistor bank.

Numerous other loading devices were considered, but this seemed to be the cheapest as well as the most useful one that was proposed, especially in view of the development work required for the others.

An electrical tachometer was direct-coupled to the generator shaft. The voltage from this tachometer actuated an indicating and recording instrument and also a special relay which would trip the solenoid valve in the compressed air inlet to the turbine. It was so arranged that the valve would be automatically tripped shut if the speed should become excessive, for an obvious reason, and also to trip the valve if the speed should become too low. This latter provision was an attempt to safeguard against the condition of a failure of the coupling or gear, since in the event of such a failure the generator would promptly slow down.

Experimental Expander

In order to prove the most questionable points in this proposed design as described, an experimental turbine was planned for operation on room temperature dry air. The doubtful points which were to be explored were:

1. The operability of the shaft assembly.
2. The oil seal.
3. The nozzle efficiency.
4. The wheel structure and mechanical strength.
5. The general assembly.
6. Efficiency.

Attainment of consistent efficiency results between the warm air and the cold air condition was not subject to serious doubt.

With these factors in mind, an experimental turbine as shown in Figure 45 was built. The turbine

FIGURE 45. M-5 unit—parts of large turbine expander.

was designed to operate at an expansion ratio which required the same wheel tip speed as would be required for the cold air. No essential difference in the nozzle design between the warm and cold air was necessary, and the warm air nozzles were made identical in design and dimensions to those planned for the final cold air unit. Different materials, however, were used. The turbine case, seals, shaft, bearings, and turbine supports were also made identical with corresponding parts planned for the final unit. The turbine wheel was of the same diameter and had the same blade and peripheral width as the wheel in the final proposed unit. The wheel passages and wheel discharge area had to be different in order to correspond with the volume variation under this somewhat different condition and this was accommodated by alteration of the wheel profile. The air supply, on which the turbine operated, was dried by passing it through a large anhydrous calcium chloride bed, and its pressure controlled by a Fisher regulator. The turbine case was insulated and the efficiency was measured by temperature difference between the inlet and discharge. In order to minimize the error due to cold loss, the discharge was run at an elevated pressure so as to increase the throughput of air. The loading device consisted of two 5 kw d-c generators belted to the turbine wheel.[22]

The turbine efficiency was measured at various pressure ratios and at various turbine speeds. The results of a typical set of these data are shown in Figure 46, wherein efficiency is plotted against the ratio of kinetic energy at wheel tip speed velocity to total expansion energy of the air. These tests proved the points enumerated above, and in the final unit the parts were duplicated in suitable anti-embrittlement material. The wheel profile was necessarily changed to correspond with the volume changes that would occur under the low temperature conditions. It was not expected that any perceptible difference would be found.

During the testing of the warm air unit, it was requested that a study be made to determine how small these turbines could be built. The doubtful point in this study was the nozzle efficiency, so a special nozzle ring with three times as many nozzles one-third as large was made to fit into the warm air turbine. The minimum throat dimension in this new set of nozzles was about $\frac{1}{16}$ in. The efficiency of these nozzles was lower than that for the larger ones which themselves were quite small, but the difference was barely measurable and it indicated that an efficient small turbine could be built.

PERFORMANCE OF FINAL UNIT

After a few initial minor difficulties were overcome, the performance of the machine has been completely satisfactory, and a total operating time of over 1,100 hr has been accumulated.[34] Low-temperature

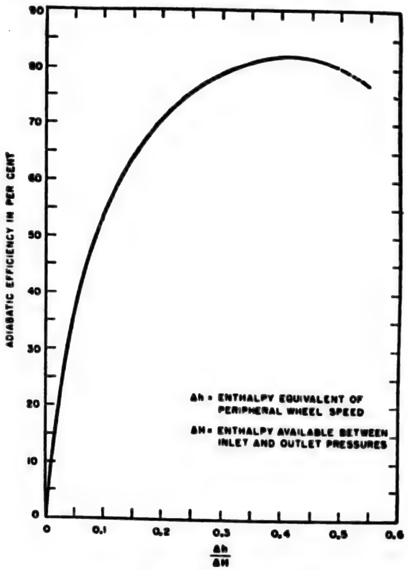


FIGURE 46. Turbo expander efficiency.

tests have produced the results shown in Figure 47, in which expansion efficiency at optimum speed is plotted against expansion energy per pound in the cold air.[26,27,30,31,32,33] This confirmed the expectation of little or no difference between warm and cold performance. It was not expected, however, that the curve would be as straight and flat as it is, and some inefficiency in the wheel discharge is indicated. Estimated operating characteristics of the machine are shown in Figure 48.

Mechanically the turbine has operated very well. There has been no noticeable wear except on the pinion of the reducing gears, which quickly became

pitted at the pitch line but which is still operating satisfactorily. The ball bearings have remained in perfect condition; the shaft ball bearing carries a thrust load of about 300 lb at 22,000 rpm, and one of two ball bearings supporting the pinion gear is similarly loaded.

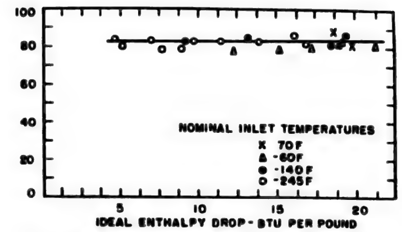


FIGURE 47. Expander efficiency at optimum speed.

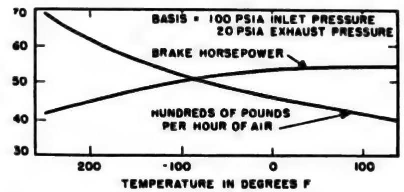


FIGURE 48. Operating characteristics of large turbo expander.

Initial difficulties include (1) overheating of the shaft ball bearing, (2) excessive oil frothing, (3) external oil leakage from the shaft, (4) severe nozzle erosion, and (5) low air capacity. The bearing overheating was caused by churning in a pool of oil, and the condition was corrected by eliminating an oil pocket. The oil circulating system was revised to handle the oil froth, but the frothing condition has not been encountered in normal operation with cold air; the earlier condition probably resulted from contamination of the oil with water during preliminary testing with warm, undried air. A minor revision practically eliminated the oil leakage. The nozzle erosion was eliminated by substituting nitrided stainless steel for the original mild steel, and enlarging the nozzles corrected the low capacity. In addition, there was one unexplained sleeve bearing failure, and a second failure caused by a breakdown in the auxiliary lubricating oil system.[26,27]

It should be possible to build such a turbine to operate at an efficiency of 87 or 88%; thus, losses amounting to 5% in this machine could probably be eliminated if a considerable effort is made to do it. The major portion of this preventable loss is probably in the wheel and in the wheel discharge. The wheel passages are not nearly as smooth as they could be made as the result of foundry experience in making these wheels.

A reapplication of the methods used in selecting the wheel speed and wheel dimensions if based on more accurate data on the individual losses within the turbine would probably indicate a somewhat different size of wheel and thus result in a slight increase in efficiency.

As a result of this study it appears as though the turbine can be built in any size larger than about 250 lb of air per hr, and that in any but the smallest sizes the expansion ratio could be considerably larger than has been used in this unit.

5.11.2 Small Turbo-Expander Capacity 290 Pounds of Air per Hour

A turbo-expander to handle 290 lb of air per hr would meet the refrigeration requirements of a 1,000 cfh mobile gaseous oxygen producer.[34] As finally built, such an expander including its loading mechanism was but a fraction of the weight and size of the reciprocating expander for the same duty (compare Figures 37 and 49). Perfection of this expander together with successful development of a high-speed rotary compressor (Lysholm compressor, Section 5.4) were enticing goals which would result in extreme compactness and lightness in weight for oxygen production equipment.

Because of the considerable interest in portable oxygen plants, it was desirable to ascertain the lower size limitations of this type turbo-expander. Small machines are generally less efficient than large ones, but many of the power losses originate in comparative inaccuracies and comparative roughnesses of passages. This type expander is quite simple in design so that additional care and attention to these factors would not be unreasonable. It was hoped that a rather small unit might have acceptable efficiency.

It had been found possible to build efficient nozzles in small sizes so the possible source of greatest energy loss was already known to be insignificant. The

design experience from the large expander was extrapolated into the small size and this indicated a rotational speed of about 80,000 rpm, an impractical speed. A two-stage expander was then studied where half of the enthalpy drop took place in each wheel. This gave a machine which needed to rotate at just under 50,000 rpm, which speed was considered possible. A shaft seal for this speed was not considered to be practical, but it was presumed that a worm gear could operate under pressure to reduce the rotating speed to 3,600 rpm, and then a seal could be put on the 3,600 rpm shaft.

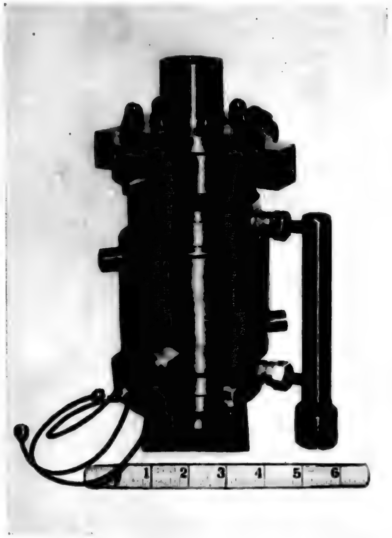


FIGURE 49. Two-stage turbine expander with electric generator.

In spite of the apparent feasibility of the gear, it proved to be a difficult design problem and was abandoned in favor of a generator-type loading device, which had the following salient advantages:

1. The generator bearings acted also as the turbine bearings.

2. It was possible to build in a self-contained lubrication system.

3. The load could be varied over wide ranges and an estimate of its value read from electrical instruments.

4. The frequency of the generated current was a direct measure of the speed.

5. The size was reasonable.

The first model, which never proved entirely satisfactory, consisted of a rotaing element mounted in two high-speed ball bearings between which was located a $1\frac{1}{4}$-in. diameter Alnico magnetic rotor, and two turbine wheels mounted on the end of the rotating shaft and overhanging the bearing about 2 in.[28,29] This 2 in. of shaft was sufficient to reduce the cold loss to a tolerable amount. The generator stack was 3 in. long and had a two-pole three-phase winding. The stator case was attached to the turbine case by means of a thin-walled cylinder. This thin-walled cylinder joined the warm generator and the cold turbine and cold losses through it likewise were small. The whole unit was supported by attachments to the turbine case. The arrangement may be seen in the accompanying Figure 50, and a photograph is shown in Figure 51.

Although the critical speed of the shaft was estimated on the basis of actual flexibility measurements to be above 64,000 rpm it would not run satisfactorily above 40,000 rpm and was at times rough at that speed.[29] This was considered to be due to the dual purpose served by the bearings, so the unit was revised to include a third bearing. Two of the bearings then supported the heavy rotor magnet and the third bearing gave guidance to the turbine shaft. This arrangement eliminated the shaft run-out difficulty. It has a calculated critical shaft speed in excess of 100,000 rpm.

LUBRICATION

Oil was transported to all three bearings by means of a circulating stream of air. The lower end of the shaft was drilled in such a way that it picked up oil from the reservoir into which it extended and atomized it. The resulting oil fog was circulated through all bearings by a blower effect attained by slots cut in suitable disks mounted adjacent to the bearings. Changes in pressure in the turbine caused pulsations into the closed space within the generator and except for a special provision would cause a breathing of this oil fog into the turbine. This was prevented by leading a stream of clean air from the point of highest pressure within the generator to a lantern ring on the overhanging turbine shaft so that clean air flowed from that point into the generator at all times, and

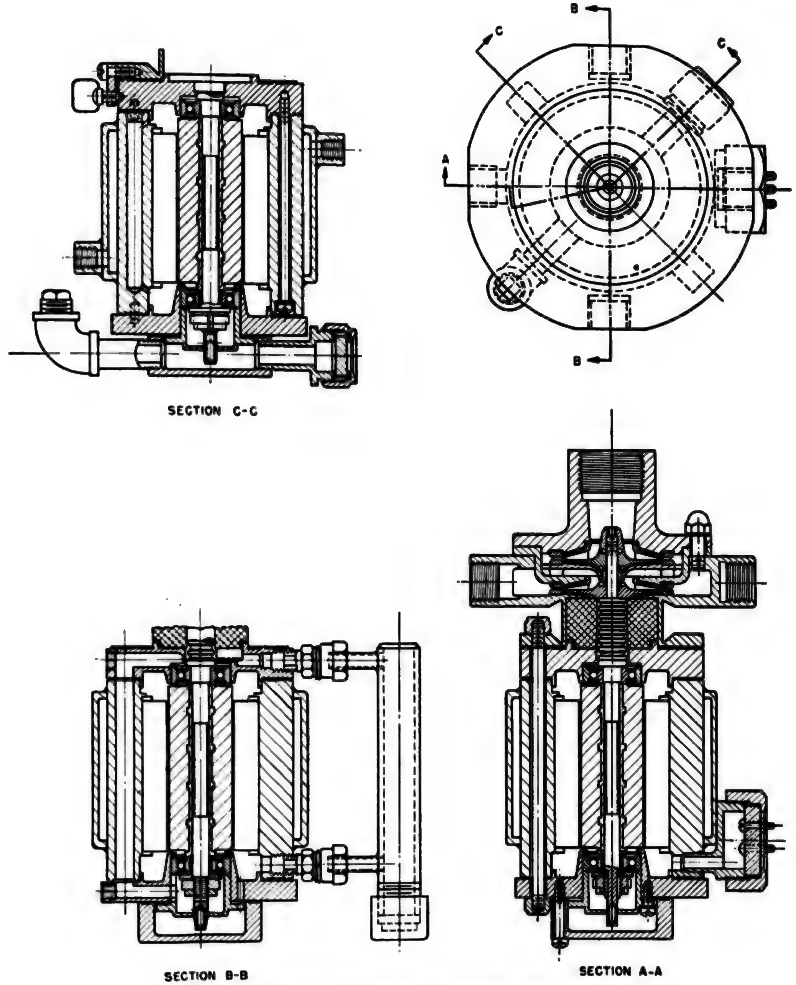


FIGURE 50. Assembly drawing of two-stage expander.

any breathing was from this supply of clean air. The air was made clean by bringing it through a suitable wire cloth cartridge outside the generator casing. A survey of the pressure existing at the various critical points during operation demonstrated the workability of this lubricating system.

Loading Device

The loading device consisted of a 200 v, 2 kw generator which used a permanent two-pole magnet rotor. The speed limited the diameter and the necessary generator stack length was estimated at 2 in., but for safety in the first unit, it was made 3 in. long.

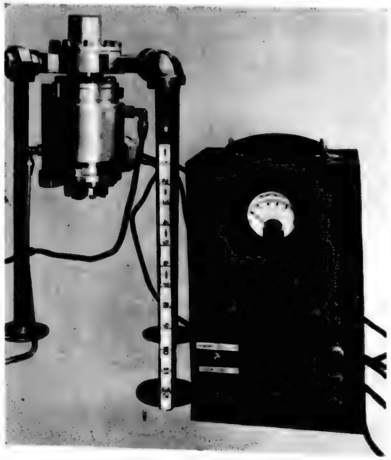


Figure 51. Two-stage turbo expander with speed indicator.

The magnet was found capable of withstanding considerable electrical abuse and was not so critical as was anticipated at first, and in fact is not critical at all.

The chief difficulty in the generator was the high inductance within the coils, which limited the possible load current. This was known to be a difficulty and it was planned to use an outside capacitance in combination with the resistance load to raise the load current. It turned out to be an easy matter to produce the required load by means of a condenser of reasonable size.

Other types of loading devices considered were the aforementioned worm gear, a direct-connected fan, and an enclosed fan. The gear, as pointed out before, proved to be less attractive when carefully examined. The direct-connected fan would require a shaft seal operating against a high pressure difference and at above twice the permissible running speed. The enclosed fan was workable except that it would not have a wide load range and would not give a measure of speed.

Speed Indicator

A special speed indicator was built which was actuated by the frequency of the generator current. It consisted of a means for discharging a condenser through an ammeter once each cycle, the condenser being charged each time to a constant voltage. It proved to be a very satisfactory speed indicator except that separate 100 v power was required for its operation.

Performance

On warm air at full rated pressure, the unit gave better than 50% efficiency, which is substantially better than that of the large single-stage unit under identical conditions. This means that its starting-up characteristics will be better than the large one, and this is due to the two-stage arrangement. It runs very smoothly and is easy to control.[34]

Fouling of the wheels and nozzles with oil has not yet been eliminated completely, and this has prevented testing the turbine under cold conditions.

The unit weighs about 25 lb and could be made to weigh half this amount, if necessary. It is estimated that the control box and load resistors occupy about 1 cu ft. The unit is considered to be easy to manufacture, to have satisfactory life, to be mechanically sound, and easy to operate. Its shortcomings will probably originate in the difficulty of maintaining its capacity because of the small nozzle passages and other passages being continually partially plugged by an accumulation of ice.

The unit requires considerable testing to determine bearing life, coil insulation life, and lubricant life. The coil insulation is subjected to rather high temperatures under considerable air pressure in the presence of oil.

Development work on this expander will continue after completion of NDRC work under Navy Contract NObs 2477 and operating results will be available from reports of the University of Pennsylvania Thermodynamics Research Laboratory operating under that contract.

Chapter 6

OXYGEN COMPRESSORS AND LIQUID OXYGEN PUMPS

By *J. H. Rushton*

6.1 COMPRESSION OF OXYGEN

One of the most important uses for oxygen to be produced by mobile equipment was for aviator breathing. It is not only necessary to have high-purity oxygen for aviation breathing purposes but it is absolutely essential to have the oxygen dry (specifications: dew point, −70 F). Low temperatures are encountered in high altitude work and it is imperative that the moisture content of aviation oxygen have a dew point so low that there would be no chance for deposition of water in the supply lines from oxygen cylinders to the aviator's mask. The conventional oxygen compressor is used to compress oxygen from approximately atmospheric pressure to 2,200 psi. This pressure of 2,200 psi is the pressure normally maintained in the oxygen cylinders used throughout industry in the United States. These compressors are ordinarily lubricated by water or dilute solutions of glycerin in water. Thus the compressed oxygen contains a considerable amount of water vapor after being compressed in a cylinder lubricated in this fashion so that, for breathing oxygen, it is necessary to install some drying device on the compressor whereby the dew point of the compressed oxygen can be brought down to acceptable limits.

Perfectly dry oxygen gas can also be charged to high-pressure cylinders by starting with liquid oxygen placed in a high-pressure vaporizer where the oxygen is caused to evaporate, usually by the addition of heat from an external source, and pressure is allowed to build up in the vaporizer which can then be attached to oxygen cylinders for charging. The oxygen will then fill the cylinder, and pressures up to 2,200 psi can easily be obtained. This is a well-known commercial process and is used in this country and also in Great Britain where pressures up to 3,000 psi are normally used. By this vaporization process it is possible to obtain perfectly dry oxygen gas and thus the necessity for operating a water-lubricated compressor, as well as the subsequent drying equipment, is eliminated.

Because of a number of circumstances and tactical uses for gaseous oxygen it was desired that NDRC develop gaseous oxygen producers for the Army Air Forces and Engineer Board. Of secondary importance was the development of mobile liquid oxygen producing equipment. The next problem was whether a successful nonlubricated oxygen compressor could be developed, thus eliminating the considerable equipment and weight of a plant which would call for the conventional type of oxygen compression with a subsequent drying process.[2]

Since the section was interested also in the development of liquid oxygen producers both of small and large capacity, several vaporizers and liquid oxygen pumps[3,4,5,6,7,8] were developed for use with such plants.

Another method available for direct production of dry gaseous oxygen without the use of a gaseous compressor was the use of a liquid oxygen pump. A liquid oxygen pump is used to compress liquid oxygen within the cold box of a producing unit, and the compressed liquid is then returned through the heat exchange system of the unit so that it extracts heat from the incoming process air and is discharged at the desired high pressure (2,200 psi), in the gaseous form, at a temperature only a few degrees below that of the incoming air. Such a pump will therefore allow the production of dry gaseous oxygen and the recovery of enthalpy in changing from liquid oxygen to gaseous oxygen at room temperature. This recovery of heat cannot be achieved in the usual liquid vaporization process described above. There is a limitation to the use of a liquid oxygen pump from the process standpoint; it can be applied with good thermodynamic efficiency only to processes in which the air feed is at 250 to 300 psi or higher. Thus, the liquid oxygen pump has not been applied to the low-pressure process (that is, 100 psi and 150 psi) but has been applied with considerable success to process operating at above 600 psi.

6.2 TWO-STAGE NONLUBRICATED OXYGEN COMPRESSOR

The first attempt to build a dry oxygen compressor was in connection with a regenerative chemical unit (Chapter 11). Oxygen produced by this unit would be available at or a little below atmospheric pressure

but was to be delivered to low-pressure gas storage tanks at 150 psi. The first development was a four-stage oxygen compressor which was intended to be water lubricated.[2] The simplest method for design of the low-pressure two-stage dry oxygen compressor was to modify the four-stage water lubricated compressor by using the main crankcase, the upper crankcase, and the first and second stage cylinders. Specifications for the compressor are given in Table 1.

TABLE 1. Specifications Clark two-cylinder, two-stage 0–150 psi Dri-oxygen compressor.

Type:	Vertical, two-cylinder, two-stage, nonlubricated, water-cooled, single acting.
Model:	DVO-2-2
Compressor data	
Suction pressure	0 psi
Discharge pressure	150 psi
Maximum inlet temp	120 F
Capacity	16.6 cfm at intake conditions
Approximate bhp required	7.0
RPM	700 to 860
No. of cylinders	2
Bore	5 in. and 3.5 in.
Stroke	3.5 in.
Design features	
Cylinder	Highly polished chromium-plated bronze
Piston rings	Segmental graphitar No. 2 carbon
Dimensions	
Installation drawing	103-50
Overall length	26 in.
Overall width	20 in.
Overall height	35 ½ in.
Approximate weight	400 lb.
Accessories supplied	Oil pump and oil pressure gauge, water piping and flywheel grooved for V-belt drive

Special pistons replaced those of the tandem design. Except for the absence of the third and fourth stages and the addition of new cylinder heads, the new machine was identical with the original. Figure 1 is an early view of the first two-stage unit, and Figure 2 is a cross-sectional drawing of the two-stage machine.

Data on the performance of the unit were collected under varied operating conditions during a total of 75 hr of actual test work. The data and mechanical operation were carefully checked as the experience gained was expected to be of considerable value in connection with the work on the four-stage machine. Figures 3, 4, 5, and 6 are illustrative of the performance of the two-stage compressor.

All tests utilized air as the test medium, since at that time a supply of oxygen was not at hand. It was thought that this would not introduce a serious error in the work because of the similarity of the thermodynamic properties of air and oxygen.

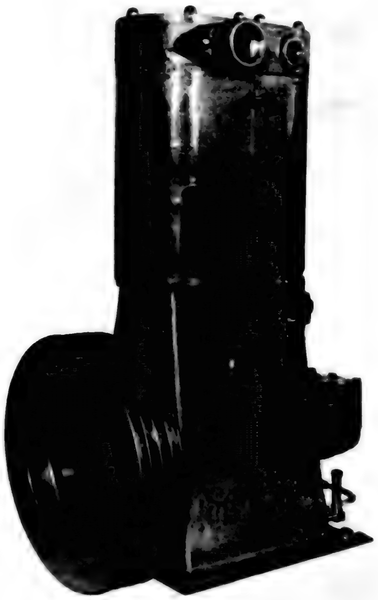


FIGURE 1. Vertical two-stage dri-oxygen compressor.

The test runs brought to light a number of minor difficulties and troubles which were corrected. No serious mechanical difficulties were experienced and the carbon rings showed no evidence of undue wear.

The design shown in Figure 2 is simple and conventional. The only innovation was the segmental carbon rings operating on a heavy, bright polished, chromium-plated cylinder liner. Figure 7 shows a closeup of a set of carbon rings typical of those used on the oxygen compressor on the first and second stages.

Of this type, only two machines were built. The first was incorporated with the Salcomine oxygen generating plant (Chapter 11) aboard the USS

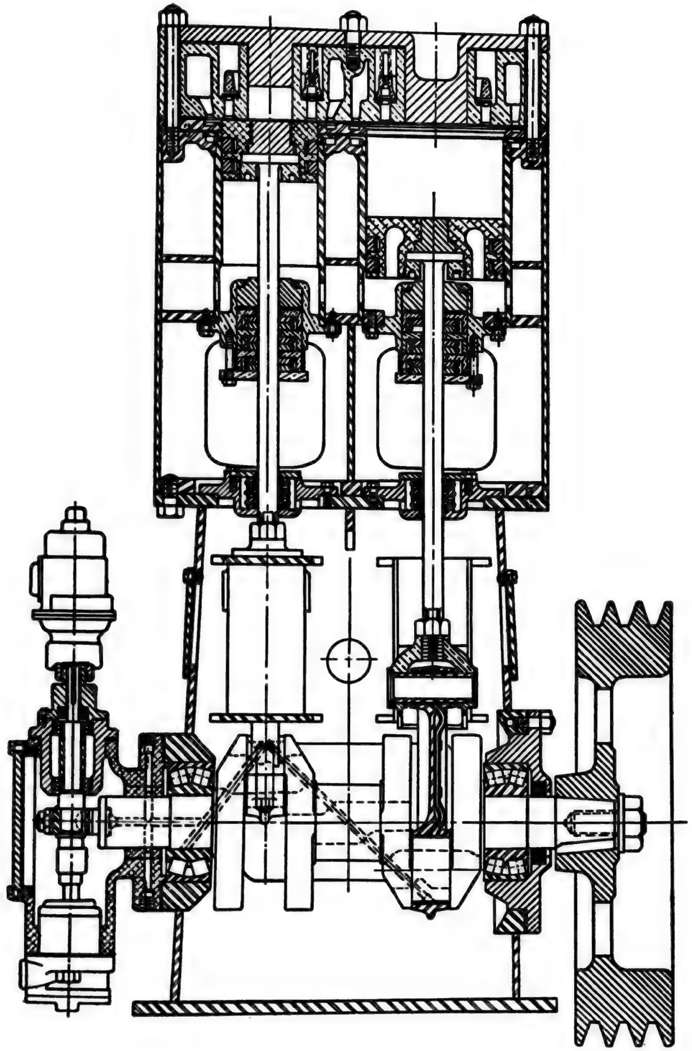


FIGURE 2. Cross-section of two-stage 3½-inch stroke dry oxygen compressor

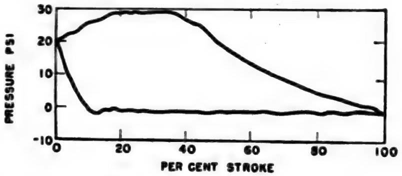


FIGURE 3. Two-stage dry oxygen compressor pumping air at 700 rpm, 150 psi discharge typical low-stage compressor card.

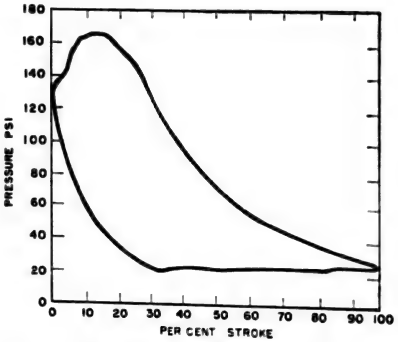


FIGURE 4. Two-stage dry oxygen compressor pumping air at 700 rpm, 150 psi discharge typical high-stage compressor card.

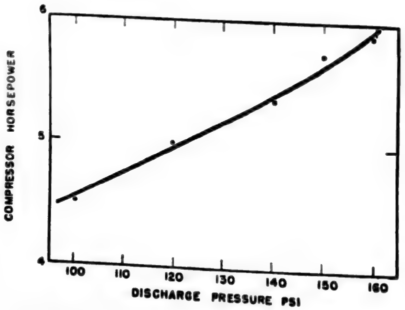


FIGURE 5. Two-stage dry oxygen compressor; indicated compressor horsepower vs discharge pressure, atmospheric intake (pumping air).

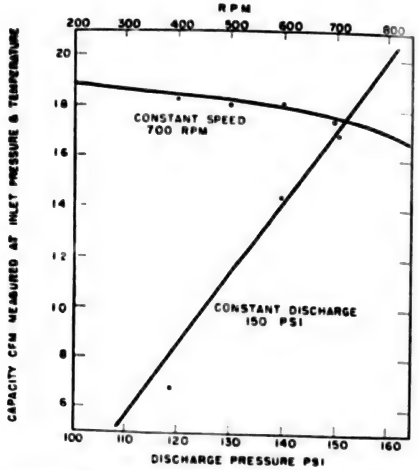


FIGURE 6. Two-stage dry oxygen compressor; capacity vs discharge pressure and rpm (pumping air).

Prairie, a Navy destroyer tender; the second was delivered to the Central Engineering Laboratory in Philadelphia.

6.3 FOUR-STAGE NONLUBRICATED OXYGEN COMPRESSOR

In the early work on development of oxygen compressors it was felt that there would be little chance of success for building a nonlubricated oxygen compressor for delivery at 2,000 to 2,200 psi.[2] Accordingly, the first oxygen compressor was designed to be water-lubricated using micarta rings with polished chromium-plated brass or bronze liners. A machine for water lubrication was built and underwent many hours of test work. Meanwhile the two-stage low-pressure nonlubricated compressor described in the previous section was built. The test runs were so satisfactory that it was believed that a successful nonlubricated four-stage high-pressure compressor could be designed. During the development of the oxygen compressor a considerable effort was put forth to convert the water lubricated four-stage machine into a nonlubricated machine. This was a difficult undertaking but it is now felt that the development has been largely successful and although the machines

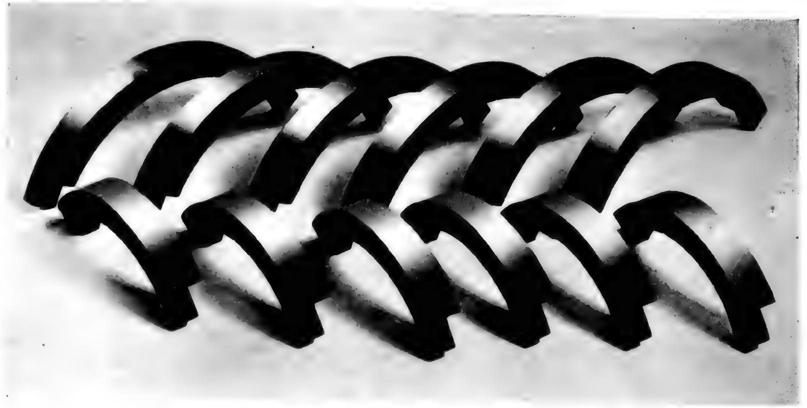


FIGURE 7. Carbon rings used on two-stage dry oxygen compressor.

do not as yet have as long a ring life as desired, relatively little further development should be needed to make possible a nonlubricated oxygen compressor which will have as long a life as the commercial compressors available before the war. The compressor is compact and light in weight compared with commercially available machines. The program on the water-lubricated high-pressure oxygen compressor was never completed but was a part of, and merged with, the nonlubricated one. To quote from the Clark Brothers report, "Of all the projects covered by contract OEMsr-370, the development of a satisfactory portable oxygen compressor is the one which involved the most work, tedious attention to fine details, and many discouraging failures." The specifications for the final nonlubricated high-pressure oxygen compressor are given in Table 2.

The investigations relative to this compressor were hampered and delayed by many factors, some of which were caused by a failure to understand the variables involved and others of which were the result of material shortages. The project involved the testing of many and varied materials, some most difficult to obtain. The test work running from May 1942 to May 1945 necessitated almost continual operation of two or more test compressors in order to cover the investigations required.

The project breaks down into five distinct phases or sub-projects, each of which advanced the knowledge of the subject toward a clearer understanding.

TABLE 2. Specifications Clark four-stage, 0–2,200 psi, vertical Dri-oxygen compressor.

Type:	Vertical, two-crank, four-stage, tandem, single acting, nonlubricated, water-cooled.
Model: DVO-2-4	
Compressor data:	
Suction pressure	0 to 10 psi
Discharge pressure	2,200 psi maximum
Capacity	12 to 14 cfm at 14.7 psi and inlet temperature
RPM	860
Approximate bhp	25
Stage	1 2 3 4
No. of cylinders	1 1 1 1
Bore	5 in. 3½ in. 1⅝ in. 1$\frac{1}{16}$ in.
Stroke	3½ in.
Design features:	
Cylinder liners	Highly polished chromium-plated bronze
Piston rings	Segmental Graphitar 2 and Stackpole carbon H4-WA
Dimensional data:	
Installation drawing	103-157
Overall length	28 in.
Overall width	19½ in.
Overall height	63¼ in.
Approximate weight	650 lb
Accessories supplied	Oil pump, oil gauge, water piping and flywheel grooved for V-belt drive

The major premise was that any compressor built for the NDRC oxygen generating units should be a dry unit, that is, one which would operate without liquid lubrication. Most specifications for complete generating units provided that the oxygen charged

into cylinders should have a dew point of —80 F. If a water-lubricated compressor were used, bulky drying equipment would be necessary and it would be difficult to ascertain the quality of the drying. Some time, however, was devoted to a water and then a soap-and-water-lubricated compressor. However, a water-lubricated carbon ring compressor was soon found to be undesirable from the mechanical point of view as well as impractical from the standpoint of maintenance of standard dryness, and the sights were again set for the nonlubricant unit.

The first phase of the work centered around a pilot model, single-cylinder test machine which served its purpose well in helping to define the type best suited for preliminary work. Several preliminary arrangements were tested and found to be unsatisfactory.[1]

The second phase covered the modification of the original full four-stage compressor, which may be said to have established the conditions for the third phase of the work. This work, the last on the original machine, was a complete investigation of the effects of piston ring design on ring wear in the fourth stage of the model. It might be noted that the first and second models of the original four-stage machine differd only in the positions of the third and fourth-stage cylinders in relation to the first and second-stage cylinders. This portion of the work also set the dimensions and general design of the first production model as used on the production generating units LP-1, LPS-2, and LPAS-3 (see Chapter 3).

The fourth phase of the work covered the initial investigations on the production model. It consisted of determinations of the operating characteristics and faults of the machine. This work finally brought to light the "bugs" which had been causing the difficulties on all earlier models.[2]

With the discovery of the basic problems, the fifth and most fruitful phase of the work unfolded.

Single-Cylinder Tests. At the time the work was started, certain definite ideas had been put forward as to the general design features desirable in a dry portable oxygen compressor. It was to be a four-stage unit, preferably with two cranks, in tandem, that is, with two or more pistons operating from one crank-throw. For the first two stages, segmental carbon rings operating on polished chromium-plated liners seemed to be within the realm of practical possibilities and would not be too great a gamble. However, the route to be followed for the third and fourth stages was very difficult and it was decided to try to determine the optimum design for these stages by operating a single-cylinder pilot machine. In so doing, the design work on the first and second stages could then be pushed ahead and the complete machine prepared for whatever design was decided upon. Further, by this method, any number of combinations could be quickly and easily tried out.

The pilot device consisted of a modified garage-type air compressor having a $3\frac{1}{2}$-in. stroke and a cylinder casting adapted so that interchangeable liners of 1-in. bore could be installed. The piston of the basic air compressor was used as a crosshead and arranged so that various types of 1-in. diameter plungers and pistons could be connected to it. Both liners and pistons could be changed easily and several different combinations were tried.

By use of this device, the following combinations were investigated.

1. A solid metal plunger operating in a graphite carbon liner. The results were extremely poor as the liner wore rapidly both from gas erosion and actual friction with the plunger.

2. A silver impregnated carbon liner with a solid plunger. The results were about the same as in No. 1.

3. A solid metal plunger operating in a brass liner using a water-lubricated graphite packing. Several different arrangements of lantern and regular rings were used. However, the results were not too satisfactory and the introduction of water lubrication involved considerable difficulties in the lubrication of the crankcase parts; consequently the work was dropped.

4. A solid plunger operating in a brass liner and leather packing rings with water lubrication was tried. This, too, was dropped since considerable difficulty was experienced with embrittlement of the leather as it dried out between runs.

As a result of work on the single-cylinder pilot compressor, the decision was made to go ahead and build up a complete four-stage oxygen compressor. The design was to be such that either a water-lubricated or a dry machine could be made from the parts, the basic crankcase and running gear remaining the same. It was decided to build five complete units, holding up all parts which might have to be changed as a result of later investigations. It had been all too apparent in work on the single-cylinder pilot machine that only part of the problems developed during the test work, and that to find the true results, conditions more nearly similar to actual operation would have to be maintained.

Original Four-Stage Compressor Type I

It was assumed that the first four-stage compressor could be built with conventional segmental design carbon rings, operating against polished chromium-plated liners in the first and second stages, and that the last two stages could be changed and experimented with until a satisfactory combination was found.

The machine which finally evolved was quite similar to Figure 2 except that provision was made for mounting the third and fourth stage cylinders on top of the first and second stage cylinders. Figure 8 shows the cross section of the production model and Figure 9 is a view of the production model. The running gear is conventional, the only innovations being in the welded steel crankcase (used for lightness) and the use of the carbon rings.

The machine was so arranged that the type of material in the liners, plungers, and rings of all stages could be varied quite easily.

Following the assembly of the first two machines, more work was put on the third and fourth stages, as it was soon apparent that the first two stages were generally satisfactory for the material combinations tried. Briefly noted below are the combinations tried on the last two stages, classified under the material used on the first two stages.

1. With no lubrication; using segmental carbon rings on first two stages.

   a. Third and fourth stage carbon liners using solid chromium-plated plungers. This arrangement was discarded due to rapid gas erosion of the liners with a consequent loss in capacity.

   b. Third and fourth stage carbon liners with carbon packing rings at the base of the liners again using a chromium-plated solid plunger. This arrangement, too, had to be discarded because of rapid wear and seriously reduced capacity.

   c. Brass liners on the third and fourth stages, with various combinations of brass, steel, chromium-plated steel, and various steel rings. In each case, the heat generated was of such a magnitude that the rings were annealed and collapsed. The wear on the liners was quite severe. This combination was dropped also.

2. With water lubrication; using Micarta rings operating on chromium-plated first and second-stage brass liners.

   a. Solid Micarta plungers having annular grooves, using water lubrication. Serious leakage of water into the crankcase of the

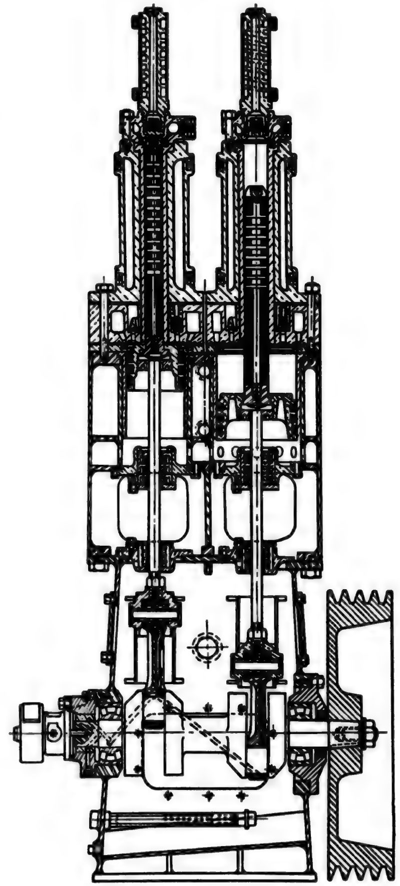


Figure 8. Cross section of final version production model, four-stage Clark Dri-oxygen compressor.

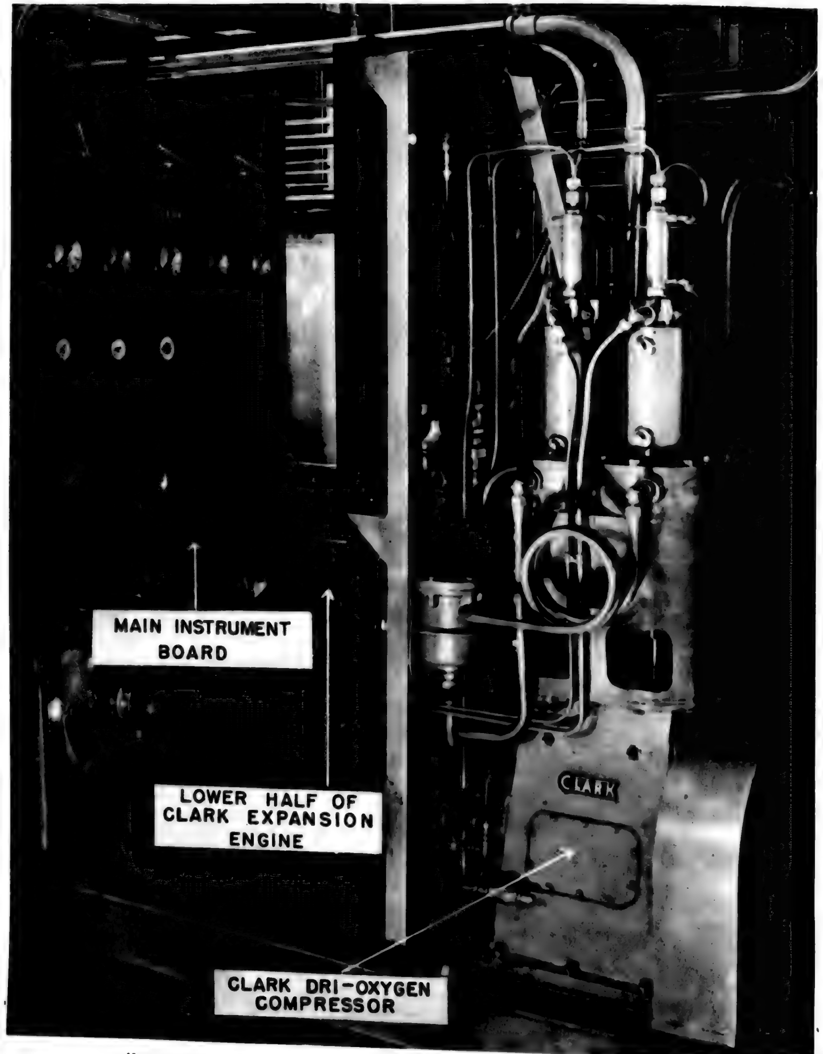


FIGURE 9. Clark Dri-oxygen compressor on model LPS-2 oxygen generating unit.

compressor resulted but was easily corrected. Severe wear on the third and fourth stage liners resulted in rapidly diminishing capacity, such that, in 20 hours, near zero capacity resulted. Machine was found to be dangerous as it caught fire easily even when pumping air.

b. The same combination, using soap and water as a lubricant with no reduction of wear and considerable difficulty caused by gummy deposits on plungers, rings, and valves.

c. Micarta rings operating against brass cylinders, with both water and soap and water lubrication. Results were good as to capacity, but mechanically the machine was poor, and it was a serious fire hazard.

3. With no lubrication; using carbon rings on the first and second stage cylinders operating against chromium-plated brass liners.

a. Carbon rings for both third and fourth stages were operated against plain, polished brass cylinder liners. The wear characteristics resulting were extremely poor since the brass was not hard enough to allow polishing of the rings.

b. Chromium-plated third and fourth stage cylinder liners were then tried using graphite bronze rings, but ring wear was considered excessive and this material was dropped.

c. Carbon rings operating against brightly polished chromium-plated third and fourth stage liners were by far the most successful combination to this date, although results were rather difficult to duplicate.

Following on the last combination, most of the work centered on refinements in the design of the carbon rings on all four stages and improvements in the surface finish of the chromium-plated bronze liners. The results of previous test work had been convincing enough to warrant standardizing on highly polished heavy chromium-plated brass or bronze liners, and, consequently, every effort was made to improve the machining and finishing operations on these parts in order to eliminate inaccuracies and sources of error in tests.

Considerable work was done on the design of the rings; step-cut, butt joint, and relieved rings were tried, and several different materials as well as numerous grades of carbon were investigated. A study of the effects of fourth-stage piston ring design was made relative to fourth-stage ring wear when using carbon material. Due to the extreme variations in the nature of the materials available, the quality of the machine work, and other variables, much duplication of test work was necessary to establish whether material or ring design was the controlling factor influencing the wear. Since the object of this series of tests was to determine the optimum active life of the fourth-stage rings, only brief attention was paid to compressor performance. On each test, a rough check was made on capacity to ascertain the maximum flow.

As a result of these tests, it was discovered that certain methods of grooving the rings or relieving them would increase ring life, but it was immediately apparent that the unloading also cut the capacity greatly. It was necessary later to decrease the amount of unloading in order to restore the capacity of the machine. This, of course, again decreased the ring life.

Table 3 shows the various tests made, the designs used, and the results. Figure 10 shows details of the various ring designs used. These results served to establish certain design requirements necessary for a satisfactory unit and to give some background on carbon piston ring design. It was clear that carbon rings, if dry, could be run successfully on chromium-plated liners under the following conditions:

1. If an excess of water is not present, the presence of actual drops of water causes the carbon dust to "ball" up and score the rings. (Flooding with water permits successful operation.)

2. If operating surfaces are polished to as fine a surface as can be obtained commercially.

3. If unit ring loadings are not excessive. The actual finite values were not established although there is a decided increase in wear on the fourth-stage rings over those in the third stage.

Furthermore, an oxygen compressor using carbon rings operating dry is safe to use for handling 2,000 psi oxygen if adequate cooling is provided.

It was found that the *blow-by* on the third and fourth-stage rings was higher than had been estimated and consequently the first machine was some 20 per cent under capacity. It was, therefore, decided to redesign the entire compressor and to change

cylinder sizes in order to bring the capacity up to that needed for the various oxygen units. This redesign was, of course, necessitated by the fact that a higher capacity machine was required for the production models.

While the redesign work on the oxygen compressor was going forward, some further tests were made on the old model. These were interesting and instructive.

The suggestion had been made regarding the possibility of using a polymerized fluoro-carbon compound [TFE] for piston rings. Consequently, samples of the material were procured, rings made up, and several tests run. Following is a brief condensation from the test report on these runs.

A run was made at 2,000 psi discharge with 300 psi suction, giving the following results:

1. Hours duration — 24
2. Average discharge temperature — 300 F
3. Test fluid — Air
4. RPM — 900
5. Ring wear
   a. Bottom 2 rings completely gone.
   b. Next 4 rings worn to 0.070 in. radial thickness.
   c. Top rings in fair condition.

It was concluded that the top rings had never made a complete seal with the cylinder wall, and consequently had not worn. Investigation disclosed that

TABLE 3. Type I oxygen compressor carbon ring life tests.

No.	Hr	Wear in. per hr	Ring material	Ring size and design	Notes
I-3	87	.0006	Graph. 2	3/8 in. ID butt joint 5A	Maximum capacity 11.0
I-4	60	.0008	Graph. 2	3/8 in. ID butt joint plain 2A	Hardened CI liner 8.0
I-5	24	.0008	Graph. 2	1/4 in. ID 1/2 in. step-cut face 4B	Hardened CI liner 5.0
I-6	12	.007	Morgan.	5/8 in. ID step-cut plain 2B	Hardened CI liner 9.7
I-6A	12	.006	Graph. 2	Top 4 step-cut plain 2B. 5/8 in. ID 4–11 grooved 1B	Hardened CI liner 8.3
I-13	48	.00045	Graph. 2	3/8 in. step-cut plain 2B	Variable disch. 12.0
I-14	22	.00013	Graph. 2	11/16 in. ID one piece 2C	Variable disch. 15.7

Notes:

1. A total of 16 tests were run in this series totaling over 1,200 hr. The balance, not shown, and totaling 200 hr were abortive and since they have no bearing, they are not presented.
2. Wear, in. per hr, represents average radial wear or reduction in radial thickness of the three segments of the top ring.
3. All tests run at constant discharge except as noted.
4. All tests run on bright chromium-plated bronze liners.
5. All tests run on *dry* air, dew point not known.
6. All rings were 7/16 in. thick except as noted.
7. Materials: Graph. 2 — Graphitar 2, U. S. Graphite Company; Morgan. — Morganite Grade 8762, Morganite Brush Company.
8. Figures shown under notes indicate maximum capacity cfm.
9. For ring styles, see Figure 10.

Tests on TFE Material. Fourth-stage rings only were fabricated and tested. The dimensions of rings on installation were in every case 0.0625 in. ID, 1.062 in. OD, and 0.437 in. thick. All tests were made on the Clark-NDRC, four-stage oxygen compressor having a highly polished chromium-plated brass fourth-stage cylinder liner. The compressor was operated at 900 rpm.

The first trial run was made with a discharge of 2,000 psi and a suction of 400 psi on this stage. Immediately following the start of the test, the discharge temperature went to 480 F. The unit was shut down and disassembled for inspection.

particles of the missing rings had actually worked down past the carbon guide into the first-stage cylinder, and through the whole machine to such an extent that the carbon rings on the third-stage piston were gummed up in their grooves.

Another trial run under the same conditions indicated the same trend. Ring wear was severe, capacity fell off rapidly, and the discharge temperature was abnormally high.

General observations on the TFE material were: (1) the material was so soft that any small particles touching it could easily be forced into its surface, (2) there is evidence of a small amount of thermo-

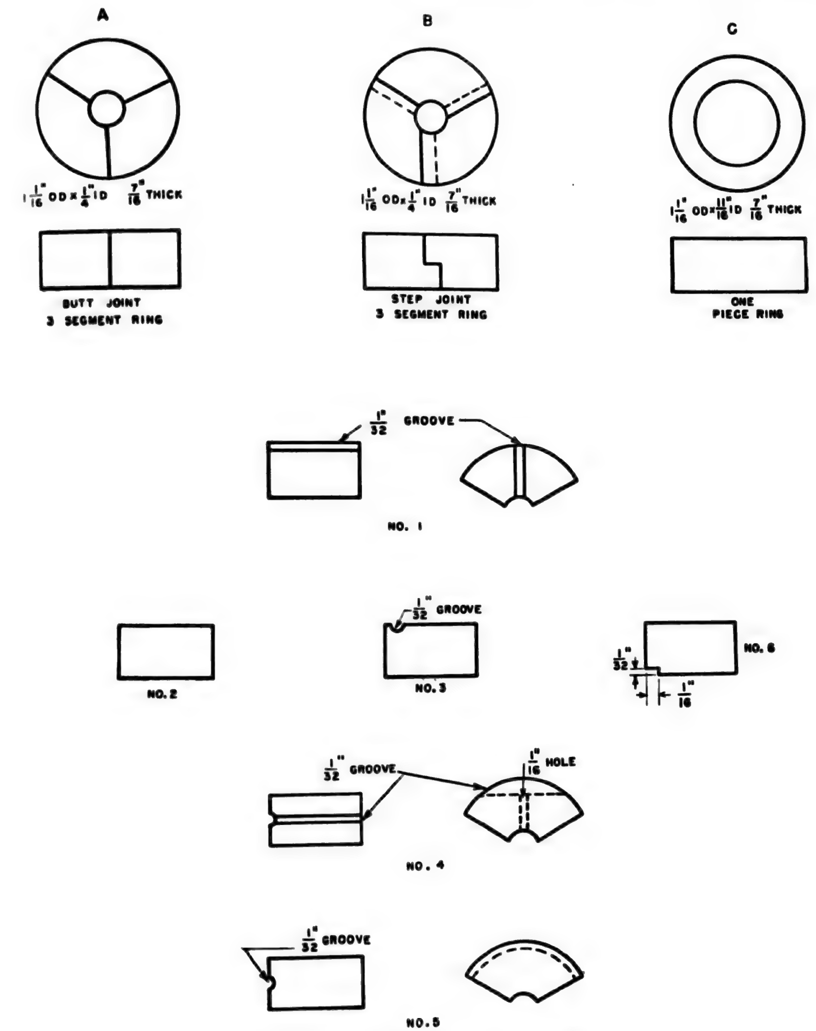


FIGURE 10. Details of experimental carbon rings.

plasticity causing binding of these rings in the ring grooves, and (3) the resistance of this material to wear is greatly inferior to that of carbon rings tested under identical conditions of operation.

These results, coupled with the information received as to the possible toxicity of the material, led to temporary discontinuance of further work on the TFE compound.

On advice that the TFE material was not toxic in the quantity which would be found in oxygen pumped by a compressor having rings of this material, two further checks were made.

Plain TFE on Wear Test Machine

	Plain TFE	Graphitar 2 Carbon
Unit load psi	60	600
Face velocity ft/min	500	500
Face temperature (metal) F	120	230
Metal surface	Chromium-plated	Cast iron
Wear rate in./hr	.036	.001

Ring Tests on Three TFE Samples in Oxygen on Oxygen Compressor

TFE Material	Results
Unmodified Dupont Teflon	Wore rapidly and flaked away
Dupont Teflon, 40% copper-filled	Collapsed under load, wore much faster than carbon
Dupont Teflon, 40% graphite-filled	Fragmented badly when cut and could not be machined into rings

Safety and Fire Hazard Test. Before finally settling on the future design two important tests were made on the old units, one to determine the safety of the design, the other to check on the actual piston arrangement. Since the original machines were to be scrapped, it was decided to test one unit to destruction. Therefore, at the close of a normal run operating on oxygen, the discharge pressure was raised to 2,900 psi, and at the end of one-half hour under such conditions, the cooling water was shut off, whereupon the discharge temperature climbed to 600 F. At this time the discharge line started to smoke and the compressor was shut down immediately. Before it stopped turning, the fourth-stage cylinder head let go violently. The peak temperature and pressure could not be observed. No flame was observed.

Upon investigation of the remains, it was found that the cylinder head was completely shattered and that the top part of the bronze piston had literally flowed into the discharge valve. The top carbon ring had disintegrated. All ferrous parts such as the valve springs and disks seemed to have burned completely. The cylinder was ripped open and the studs pulled out.

It was concluded that the general design should be safe for operation under the conditions required, provided an ample supply of cooling water was available, discharge pressures were kept under 2,300 psi, and ferrous alloys not susceptible to easy combustion in oxygen were used for valve disks and springs (one of the 18-8 stainless steels would be satisfactory).

The initial design on the four-stage compressor mounted the first and fourth and the second and third-stage pistons in tandem; this resulted in the second-stage discharge occurring while the third-stage cylinder was discharging. It was thought that better operating results would follow if the first and third, and the second and fourth-stage pistons were combined; this would mean that in every case a cylinder would be discharging during the suction stroke of the next stage.

One of the original machines was, therefore, rebuilt in this manner and the test work on it was quite detailed and elaborate. It is of sufficient importance to be considered the third definite step in the development.

Original Four-Stage Compressor, Type II

The third series of investigations on the oxygen compressor relates to the work on what came to be known as Type II of the original four-stage compressor. It was thought better to arrange the pistons and cylinders on the compressor so that the first and third, and the second and fourth stages were in tandem. To settle the question definitely, one of the original machines was so modified.

First tests on this machine indicated slightly improved compressor performance as a result of the change, and, although the improvement was only slight, it was decided to use this design on the production models then being drawn up.

At this point, it was quite evident that the key problem on this project was to find a satisfactory fourth-stage piston ring design and/or material. The rate of wear on all stages was satisfactory except on the last stage. Stated in definite terms, the situation at this point was that the Army Air Forces and the Engineer Board would be satisfied with a minimum life of 500 to 600 hr on a set of rings when operating under cylinder charging or variable discharge conditions. No standards other than these had been set, and these were based primarily on opinion. However, the tests to this date had shown a much shorter life than this for the fourth stage, with the third stage approaching this standard and the first and second bettering it.

Before scrapping this model, it was used to determine more carefully the influence of design and material on ring wear, and the actual amount of ring wear under severe operating conditions. If the machine were operated under normal conditions, that is, variable discharge as in charging cylinders, each test would take up an extremely long time, so it was decided to accelerate the test work by operating at constant discharge, 2,000 psi.

To be able to correlate the two different conditions, two tests were made using the same rings, one at constant discharge and the other at variable discharge. Actual results indicated a difference of 1 to 3 in resultant ring life.

Based on this information, it is assumed that under normal operating conditions ring life three times that found at constant discharge could be expected.

A total of twenty-five separate tests were made on this machine. The most useful data can be summarized:

1. Reduction of the ring face thickness to $\frac{3}{16}$ in. from $\frac{7}{16}$ in. apparently stabilized the wear rate at 0.00008 in. to 0.0011 in. (Tests 21 to 24.)
2. Of the three materials tested, Graphitar 2 appears to be the best.
3. Unloading the rings as in tests 21 to 24 could explain the apparent improvement over the rate shown in test 20.
4. Test 24, which had three unloaded rings at the top with eleven plain rings below, might have shown up better by reason of this arrangement.

During this and the previous series of tests, the following influencing factors were investigated to ascertain whether they were affecting the results.

1. Ring material (no really definite evidence).
2. Material of liner (no evidence).
3. Type of plating on liner (no evidence).
4. Type of finish (high polish best).
5. Carbon dust filters (little evidence).
6. Piston and ring assembly (some but no definite evidence).
7. Piston guides (found to be necessary).

6.4 CLARK DRI-OXYGEN COMPRESSOR

Probably the most instructive and thorough test work on the oxygen compressor was carried out on the production model, which was called the Clark Dri-oxygen compressor.

Early in 1944, the final design was worked out and put into production.[2] Figure 8, a cross section, shows all of the details. The general construction was little changed from the previous model, the major changes being in the size of the first- and third-stage pistons. The running gear was changed slightly but only in minor details not affecting the operation.[2] Table 2 gives the specifications of the unit.

Prominent among the changes on the new machine were:

1. Addition of solid top and bottom carbon guides on the third and fourth-stage pistons.
2. Increase in the number and decrease in thickness (to $\frac{3}{16}$ in.) of rings on the last two stages.
3. Use of beryllium copper on fourth-stage piston.
4. Lengthening of third- and fourth-stage piston.
5. Use of individual heads on first- and second-stage cylinders.
6. Lap-fitting and polishing of third- and fourth-stage liner.
7. Use of two segmental compression and one heavy segmental guide ring (all of carbon) on the first two stages.

The machine built was based on the theory that the best results would be obtained using carbon or some similar material operating dry on bright chromium-plated bronze. All test work was to be devoted to refining the design, and investigating the influence of ring design and material on the operating life of the rings.

It was found almost immediately that the results on the first two stages were uniformly good, confirming the results on the early four-stage and the two-stage dry oxygen compressor. Apparently, the unit-loading pressures are such that undue wear does not result.

Early in the work, however, it was clear that much thought and time would have to be spent on the third and fourth stages, as difficulty was experienced in duplicating results, and wear seemed to be abnormally severe.

The work on this machine can be considered in three separate categories. The first was the mechanical, the second consisted of exploratory ring wear tests, and the third covered a detailed analysis of the problems concerned with ring wear. Incidentally, the latter has been the most fruitful with definite positive results.

The first work on the machine might properly be called the shakedown period, wherein all facets of the machine performance were investigated and remedial action taken where necessary. This work,

mainly routine and necessary on most new equipment, was soon finished and deserves only passing comment. The items covered were:

1. Design changes to obtain satisfactory crankshaft material and bearing liner combination (war shortages).
2. Change-over to babbitted crossheads necessitated by reduction of lube oil flow around piston rod.
3. Material changes on fourth-stage pistons.
4. Cylinder design changes in order to drain casting completely of cooling water.
5. Addition of thermally operated alarm system.
6. Horsepower and capacity tests.
7. Ring life tests operating with oxygen on first trailer-mounted oxygen units.

Of all of these, only numbers 6 and 7 require additional comment.

Figures 11, 12, 13, 14, and 15 depict the operating characteristics of this production-type oxygen compressor when operating at its maximum design discharge pressure. The reason for checking at suction pressures above atmospheric is that it was expected it would be necessary to raise the suction pressure to counteract loss of capacity caused by ring wear.

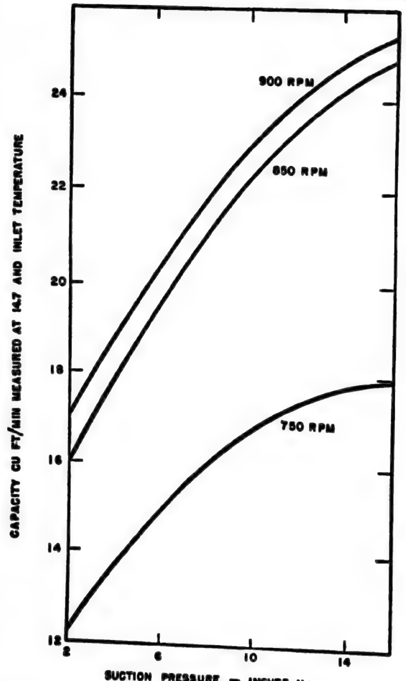


FIGURE 11. Dry oxygen compressor capacity vs suction pressure at various speeds.

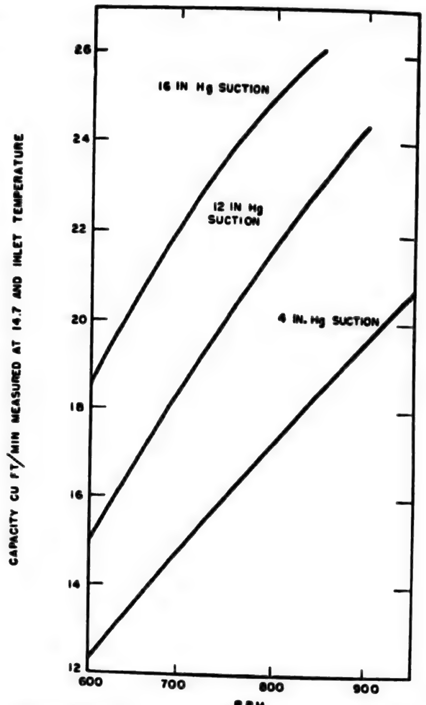


FIGURE 12. Dry oxygen compressor capacity vs rpm at 2,000 psi discharge.

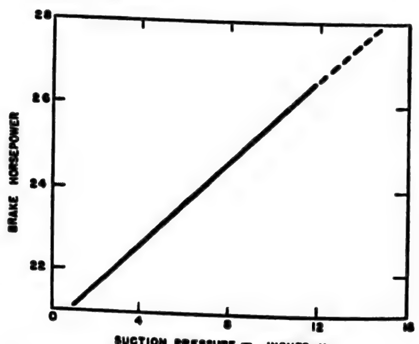


FIGURE 13. Dry oxygen compressor brake horsepower vs suction pressure at 860 rpm.

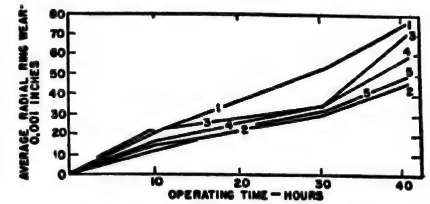


FIGURE 14. Fourth-stage ring wear, top five rings vs operating time using three-piece segmental Graphitar No. 2 (PbI_2 impregnated) (none unloaded) dry oxygen constant 2,200 psi discharge.

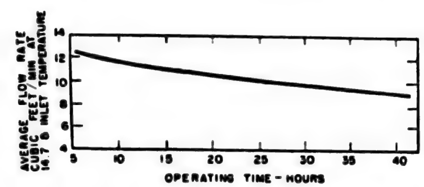


FIGURE 15. Average instantaneous capacity vs operating time using three-piece segmental Graphitar No. 2 (PbI_2 impregnated) (none unloaded) dry oxygen constant 2,200 psi discharge.

The horsepower shown by Figure 13 is at least 50 per cent over that expected for an oil-lubricated machine for these conditions. The difference can only be ascribed to increased frictional losses.

Concerning item 7 above, the first endurance test on the first production model compressor was made on one of the Model LP-1 trailer units. The fourth-stage ring life on this test did not exceed 60 hr with the machine operating under cylinder-charging conditions (variable discharge). The charging rate or capacity of the machine dropped below practical limits after 60 hr. This was far from the results obtained during the last of the previous tests detailed, where ring life approaching 250 hr had been obtained.

A long series of tests was made, varying many conditions. Filters were tried between stages, as well as operation on dry air, and in every case the ring life was found to be far shorter than previously experienced. Several methods of unloading or relieving the rings were tried, but a combination which gave reasonable wear would result in extremely low capacity. At that point it was concluded that for some reason previous tests had been in error, or that some insignificant but vital detail had been changed. To prove or disprove such conclusions, further tests had to be made.

The last work consisted of two groups of tests made on a compressor set up on a test block for ease of dismantling and assembly. The first tests in this series were made on oxygen, dry air, and atmospheric air, and were run to test out certain theories concerned with ring design and moisture content of the fluid being pumped.

The last group of tests in this series related to material investigations, ring design, and rechecking earlier work.

The following conclusions are valid for the further tests, which are all listed in Table 4.

1. No definite proof has been presented as to the difference, if any, in ring wear when pumping dry *oxygen* and dry *air*.
2. A definite difference in ring wear, at least 3 to 1, has been shown between operation on air containing moisture and dry oxygen.
3. Rate of wear on any given ring and any stated material is a direct function of:
   a. Ring design (unloading for example).
   b. Ring and piston assembly.
4. Rate of wear on any given ring and ring design is a function of ring material and/or liner material and plating.
5. Instantaneous capacity is not apparently a function of ring or liner material but is definitely a function of ring and ring assembly design.
6. Cumulative capacity is by inference a function of:
   a. Ring and ring assembly design.
   b. Ring and/or liner material as it affects wear.
7. It was quite apparent from the inspection of the tests that test C-10 represents by far the greatest advance in the search for a suitable ring material for use on these dry oxygen compressors. Army Air Forces had been experiencing extremely severe and even critical wear on the carbon brushes of the aircraft generators and motors operated at elevations of 30,000 ft or higher. As a result of investigations, it was felt that the increase in wear at higher elevations was caused by absence of moisture or decrease in

TABLE 4*

No.	Hr	Wear In/Hr	Ring Material	Ring Design	Notes
A-2	67	All gone	Graph 2	20 [2]	O_2, Variable Discharge Filters Used
A-3	90	.001+	Graph 2	20 [2]	Dry air, low flow, 14 cfm @ 9 lb
A-5	50	Very bad	Graph 2	20 [3]	O_2, N.G. Liners scored
A-6	31	.006	Graph 2	20 [3]	O_2, 13.2 cfm @ 10 lb
A-7	24	.007	Graph 2	20 [4]	O_2, Poor flow
B-1	62	.0005 to .001	Graph 2	4 [5], 2 [6], 14 [/],	-100°F Dry air Capacity good
B-2	29	.00075	Graph 2	20 [7]	-250°F Poor capacity Dry air liner scored
B-3	27	.00007+	Graph 2	20 [3]	Atmos. Air New liner Plunger broke
B-4	48	.0003	Graph 2	20 [3]	Atmos. Air
B-5	66	.0006	Graph 2	20 [/]	Atmos. Air 12.4 - 8.0 cfm
B-6	72	.0021	Graph 2	20 [/]	O_2 No Filters 20 -16.0 cfm
C-1	26	.0013	Graph 2	8 [8], 12 [3],	O_2 Uniform capacity
C-1A	14	.004	Graph 2	8 [/], 12 [3],	O_2 Uniform capacity
C-1B	9	.0014	Graph 2	8 [8], 12 [3],	O_2 Uniform capacity
C-2A	50	.0005	Graph 2	13 # 9 See Fig 17	O_2 Fair Flow Ring breakage
C-3	92	.00013	Graph 2	20 [8]	O_2 11.5 - 8.5 Moly plate liner
C-4	80	.0008	Nat'l	1 [8], 1 [/], 18 [8],	O_2 Top ring breakage 11.9 - 5.0 cfm
C-5	16	.0009	Graph 2	9 # 10 See Fig 17	O_2 Reasonable capacity
C-6	41	.002 top .001 2nd	Graph 2X	20 [/]	O_2 12.3 - 9.1 cfm
C-7	18	Bad	Graph 2X	20 [8]	O_2 High breakage All rings
C-8	85	#2 .00047	Graph 2X	20 [8]	O_2 11.8 - 8.5 cfm
C-10	142	.00049	H4-WA	20 [8]	O_2 12.0 - 6.3 cfm
C-11	57	.00098	K4-WA	20 [8]	O 11.0 to 9.0 cfm

* Ring designs are shown in Figure 16. Typical ring arrangements are shown in Figure 17. See notes on pages 109 and 112.

the amount of moisture in the atmosphere surrounding the brushes. Work along this line was considerably detailed and finally led to the use of lead iodide and barium salts to impregnate carbon of grades similar to those used in test C-4 and C-10. One of the interesting results of tests reported by a carbon company is that the presence of oxygen decreased the wear. (D. Ramadoff and S. W. Glass, paper 44-208 before AIEE meeting August 29, 1944, Los Angeles, California.)

8. Test C-3 appears, off-hand, to give an answer to the ring-wear problem. However, what had actually happened was that the special plating on the cylinder liners wore out rather than the rings; after the plating had worn through, the rings wore very rapidly. The plating was a special molybdenum coating developed by the Bell Telephone Laboratories for another NDRC problem. (It was planned also to use a stellite plating as developed by the Industrial Research Laboratories in Los Angeles, California, but no test has been made because of difficulties experienced in obtaining a smooth surface in the bore of the plated liner.)

The following conclusions were reached:

1. There may be one material and liner combination which will give the lowest absolute wear rate independent of ring, piston, assembly, or compressor characteristics.

2. There may be one piston and ring assembly and ring design which will give the optimum performance, measured in cubic feet hours, for any given material or compressor.

On run B-1, listed in the table, after 61.8 hours ring wear on the first six rings was as follows:

Segment (inches) 1	2	3	Avg. Rate of Wear First 40 hr	Last 21 hr
0.103	0.105	0.156	0.0015	0.0028
0.076	0.087	0.090	0.001	0.002
0.042	0.059	0.090		
0.038	0.041	0.057		
0.008	0.033	0.050		

Capacity at finish 15.6 cfm with 12 in. Hg suction.

3. It is entirely possible that no better material than some form of impregnated carbon will be found. For years past, various forms of carbon have been used for non-lubricated rubbing surfaces and for non-lubricated bearings. A case in point is the use of carbon for motor and generator brushes.

Naturally, the use of carbon rings impregnated with lead iodide raised the question of toxicity. Some rough checks have been made on oxygen pumped using these rings to determine the extent of contamination with lead. The following is an excerpt from the contractors' laboratory report on the first test.

Piston ring material H4-WA and K4-WA, examined spectrographically contained carbon and lead as the major materials, with traces of iron, aluminum, copper, and vanadium in order of abundance. Lack of adequate laboratory facilities prevented more than a qualitative examination of this material.

An examination of the oxygen pumped by a compressor using this material for 4th-stage rings was made by bleeding directly from the compressor discharge line without filters, 10 cubic feet of gas through three Milligan wash bottles in series. The gas flow rate was approximately 2 cubic feet per hour.

The total fluid content of the wash bottles, originally 450 ml. of 4% (vol.) of nitric acid solution, was evaporated to 10 ml., and 0.1 ml. of the concentrate evaporated to dryness on spectographic carbon. The sample of concentrate contained less than 0.0001 milligrams of lead per cubic foot.

Since the States of California, Connecticut, and the U.S. Public Health Service, state that the safe concentration limit is 0.0043 milligrams of lead per cubic foot, this oxygen should be safe to breathe. In our opinion provisions must be made, however, to trap out massive dust particles.

The generally accepted maximum permissible concentration of lead compounds in the air breathed by workmen is 0.15 milligram lead equivalent per cubic meter, or about 0.004 mg. per cubic feet. There can be no valid objection on the basis of possible health injury to pumped oxygen containing 0.001 mg. of lead per cubic feet, particularly because the breathing of this oxygen does not take place 8 hours a day for months and years while the accepted standard quoted above does contemplate such prolonged exposure.

Traces of iodine or iodine compounds accompanying the lead are of much less toxicological importance and may be dismissed as insignificant so long as their concentration does not exceed a few times the lead figure stated above.

NOTES PERTINENT TO FOURTH-STAGE RING TESTS PRESENTED IN TABLE 4

1. All tests were run at 2,200 psi discharge using highly polished chromium-plated bronze liners and butt joint 1/16 in. OD x 3/8 in. ID x 3/16 in. thick carbon fourth-stage rings except as noted.

2. Tests run using dry air, dry oxygen, or atmospheric air (dew point above +40 F). Where a temperature is given, this indicates approximate dew point.

3. Ten different ring designs were used and are shown in Figure 17 along with the basic ring from which these were evolved. The column labeled "Ring Design" indicates the number and type ring. Reading from left to right, figures presented indicate the position from the top of the piston, as in test C-4; the characters indicate that the top ring is design 8, the

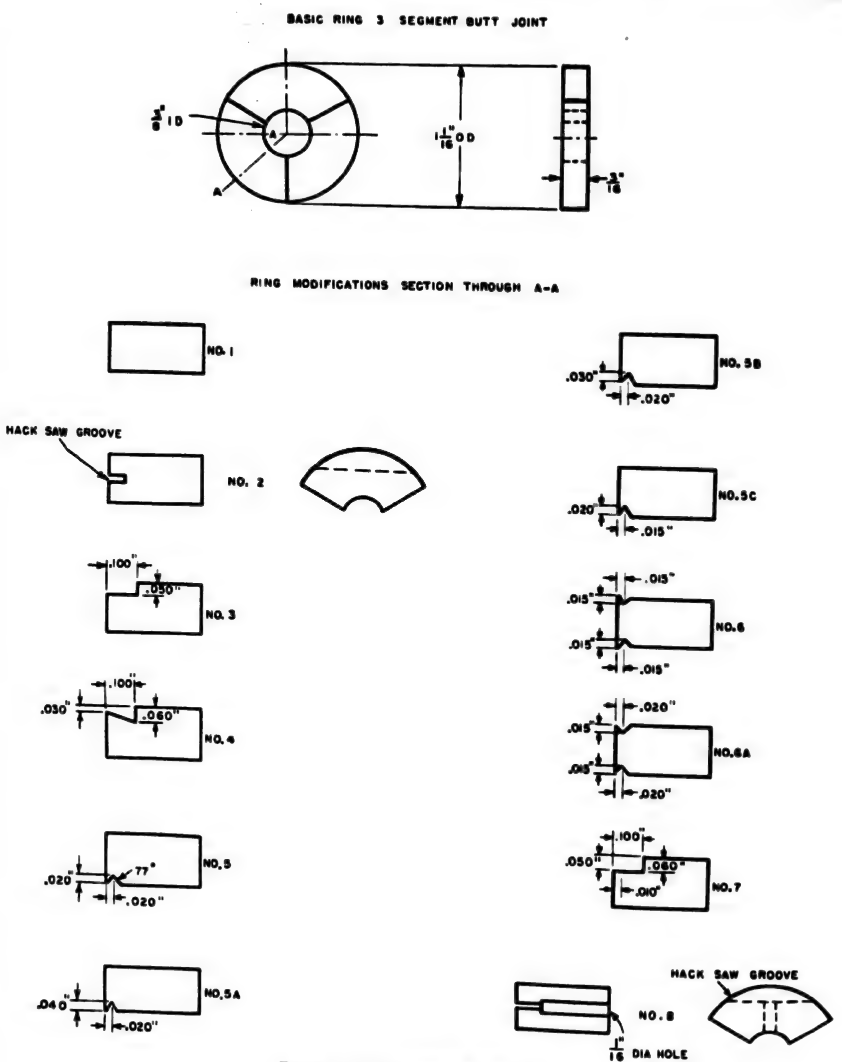


Figure 16. Fourth-stage ring design.

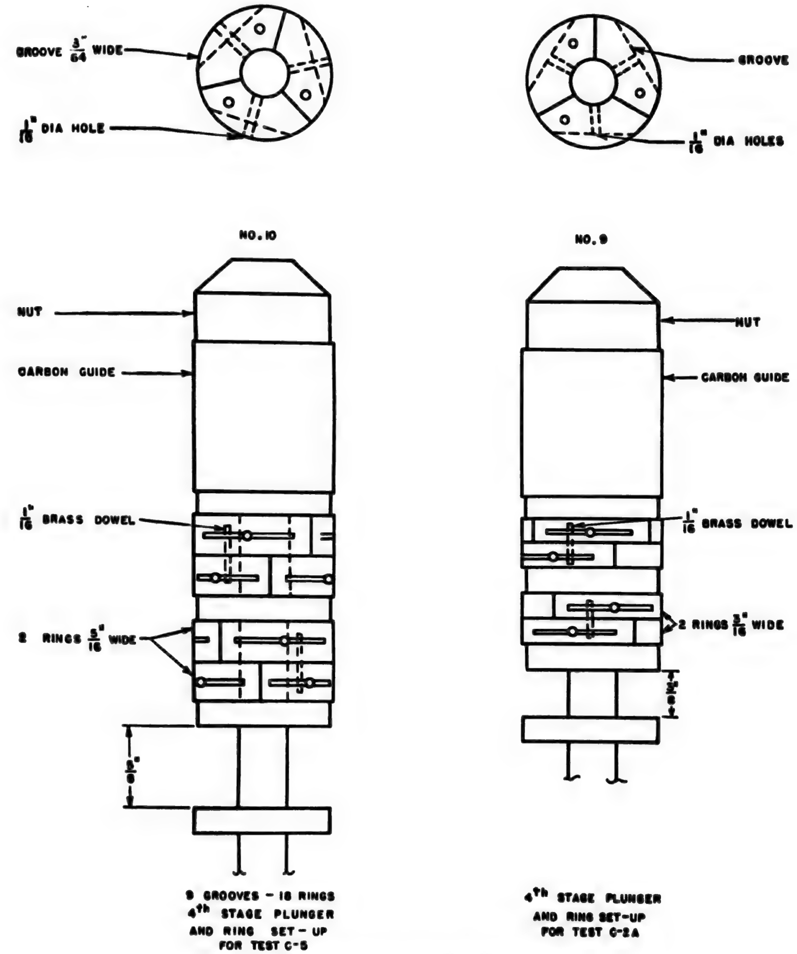


Figure 17. Fourth-stage piston ring set-ups.

second ring is design 1, while the remaining eighteen are design 8.

4. Notes indicate comments or special equipment. Capacity figures indicate starting rate and completion rate.

5. Ring wear is the radial wear or decrease in segment radial thickness. It is total wear in inches divided by total time hours run. The figure shown is for the top ring except as noted.

6. Ring materials are as follows:

Graphitar 2	Manufactured by U.S. Graphite Company
Graphitar 2X	Graphitar 2 impregnated with PbI_2 by Clark Bros. Company
National*	A graphitic carbon impregnated with barium salts and manufactured by National Carbon Company
H-4WA*	A graphitic carbon Grade H-4 impregnated with PbI_2 and manufactured by the Stackpole Carbon Company
K-4WA*	A non-graphitic carbon Grade K-4 impregnated with PbI_2 and manufactured by the Stackpole Carbon Company

* These special materials were developed by the companies shown for a special service for Army Air Forces. They have the peculiar property of wearing better than ordinary graphitic carbon where the surrounding atmosphere is practically devoid of moisture (dew points less than −40 F, for example).

6.5 LIQUID OXYGEN PUMP

In the oxygen industry it has been customary to produce gaseous oxygen of desired purity, which is then led to a compressor where it is brought to a pressure of 2,200 psi for delivery into cylinders. It appeared that considerable advantage would be secured if the oxygen compressor could be eliminated. What was desired was a high-pressure oxygen gas unit which could be used for charging cylinders directly without the use of the customary oxygen compressor. This result has been achieved by the development of a pump capable of taking liquefied oxygen from the boiler and injecting it directly into the heat interchanger system, where it emerges at any desired pressure at room temperature.

In order to produce high-pressure oxygen gas directly, it was proposed to withdraw liquefied oxygen from the boiler and introduce it into a channel of the heat interchanger system under pressure, the limit of this pressure being any value corresponding to the pressure desired in the tanks of oxygen to be charged at ordinary temperature. The change of oxygen from the liquid state to a gaseous state at ordinary tem-

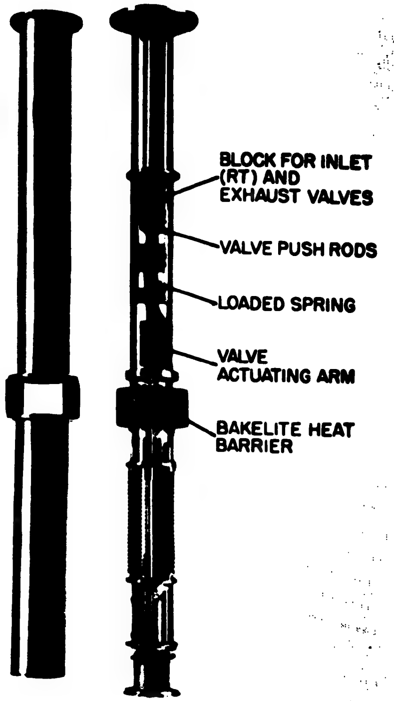


Figure 18. Liquid oxygen pump—front view.

perature and high pressure takes place in the interchanger through the interchange of heat with the incoming high-pressure air to be liquefied and subjected to fractionation. The injection has been brought about by the use of what is called for pur-

poses of designation "Liquefied Oxygen Injector Pump." The pump is operated from a branch line from the high-pressure air supplied to the unit for purposes of liquefaction and subsequent fractionation.

Details and Drawings. The pump consists of two parts, a cylinder and a piston which periodically receive supplies of liquid oxygen from the boiler for injection into the intercharge system. The force necessary to bring about the injection is obtained from a single-acting piston device without piston rod packing, actuated by the high-pressure gas. The admission of high-pressure gas to the power cylinder and its exhaustion therefrom are controlled by a valve system. Photographs of the assembled pump with the case removed are shown in Figures 18, 19, and 20.

On the left of Figures 18 and 19 are the cases for

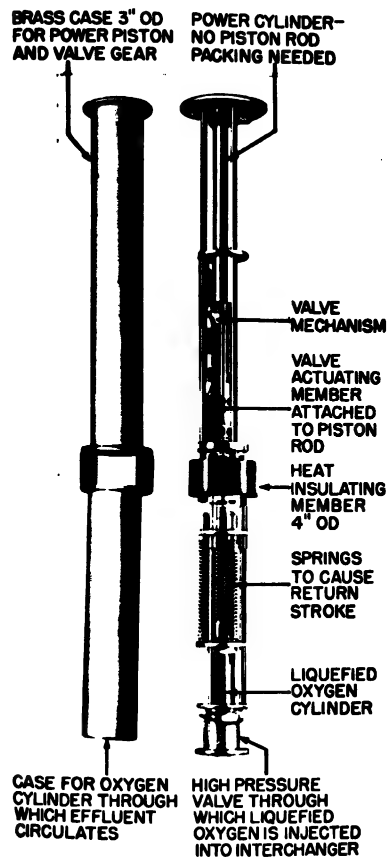


Figure 19. Liquid oxygen pump—side view.

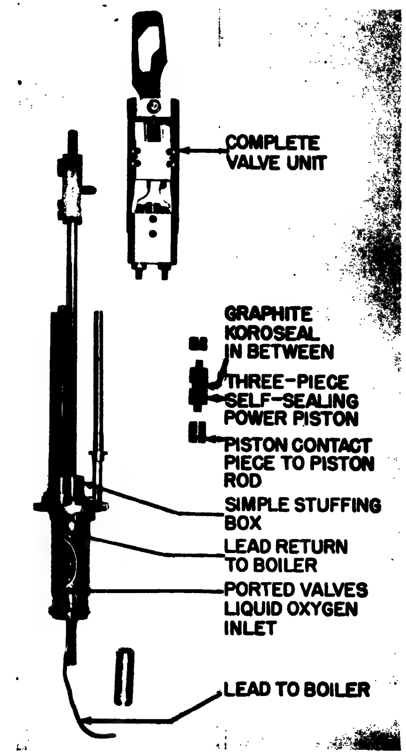


Figure 20. Liquid oxygen pump—disassembled.

the upper and lower parts of the pump. The upper part is the power end, which is designed for operation with 3,000 psi air supplied from a branch line of the inlet air to the unit. The exhaust is released within the brass case above the 2-in. canvas-backed bakelite

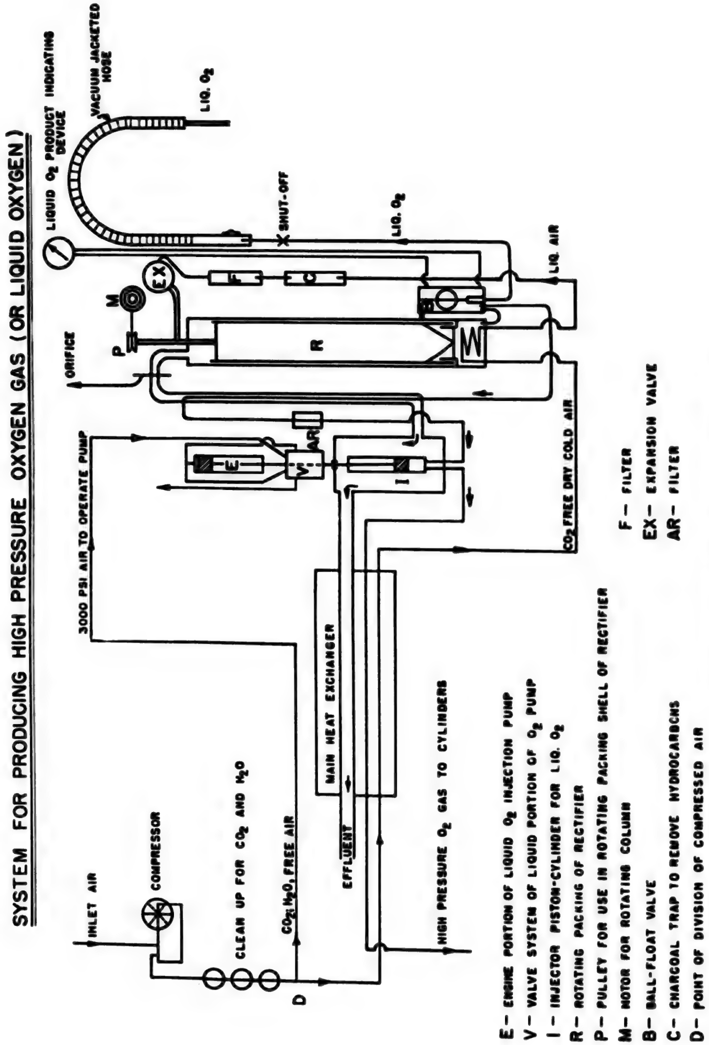


FIGURE 21. Oxygen unit with liquid oxygen pump.

member or heat barrier. The piston rod runs the length of the pump, being in contact at the power end with a compound piston represented at the right in Figure 20. The power piston operates in a liner of hardened nitralloy with superfinished surface, the body of the cylinder being brass. The pump is single acting and is therefore provided with one inlet valve and corresponding exhaust valve. Both valves are contained in the block as indicated in the figure; they are operated by push rods. Opening and closing are accomplished by pressure from a push rod mechanism, actuated by a loaded spring. The motion of the latter from one side to the other is produced by a cam and roller on the piston rod as shown. In the latest model of the pump the lever piece operating the push rods is hinged on the inlet side. This is for the purpose of holding the inlet valve open until the power stroke is complete, when a latch releases the hinged portion an instant before the exhaust valve is opened through the action of the cam. There are four springs that provide for the return stroke.

The oxygen cylinder is constructed of hardened beryllium-copper alloy. The original design of the oxygen piston has passed through several changes. Originally the attempt was made to use hardened beryllium-copper alloy with a ported valve inlet. Due to an apparently large increase in friction at —300 F for all metals investigated, this proved to be impractical. The most desirable type of piston would be one in which the leak along the clearance between cylinder wall and piston is independent of the pressure under which the oxygen is being injected into the heat interchange system. Realization of this type of piston involves some difficulties, owing to the properties of materials at low temperature.

The type of piston employed in the high-pressure drive is self-sealing on the power stroke and exhibits no appreciable friction on the return stroke. The latest oxygen piston has something of the same characteristics. In neither case is a piston packing-gland employed.

Figure 19 shows the valve mechanism as it appears for 180 degrees of rotation relative to the representation in Figure 18. Some details of the construction are shown; for example, the power piston is shown with its three parts separated. Contact between the piston rod and the piston is not permanent, the piston rod end being merely pressed against a hardened steel piece connected to one of the brass parts of the piston. Two sets of graphite rings, with the middle member of Koroseal, comprise the piston rings. The four graphite rings are soaked in light lubricating oil and provide the necessary lubrication as well as constituting suitable support for the Koroseal. The degree of contraction of the compound piston under pressure is brought about by the use of shims at each end. A spring surrounds the piston rod inside the cylinder and serves to return the piston, and also to keep the three parts of the piston in contact at all times. In the lower part of the figure the original beryllium-copper piston is shown. This is connected to the piston rod by means of a simple universal joint, a feature which has been adhered to throughout all the attempts to perfect a satisfactory oxygen piston.

Figure 21 indicates the disposition of parts of the model unit in which the pump is incorporated. This model unit is designed to produce either liquid oxygen (18 lb per hr for 300 lb per hr air circulated) or high-pressure gaseous oxygen (35 to 40 lb per hr). (See Keyes unit, Chapter 4.)

It will be noticed that the effluent line leading out of the rectifier contains an orifice and a heat interchanger for the liquid oxygen being drawn from the float chamber *B*. The purpose of the orifice is to bring about a slightly increased pressure of the liquid oxygen in the boiler relative to the pressure of the effluent. By proper adjustment of the orifice dimensions it is possible to compensate for the resistance to flow of the liquid in the line, and also the resistance due to the operation of the inlet valve to the liquid oxygen cylinder of the pump. This is a matter of great convenience in perfecting the details of loading the cylinder at the inlet stroke. The further purpose of causing this effluent to pass through the case containing the oxygen injector is to prevent *gas lock.* With a pressure in the still of some 10 psi, a potential loading pressure of approximately 16 psi can be secured through the lowering of temperature of the injector cylinder and piston. Of course the increased temperature of the effluent brought about by the cooling of the liquid has the effect of slightly increasing the heat input to the boiler.

The dimensions of the pump have been adjusted to inject 35 lb of liquefied oxygen per hr up to 1,800 psi, with operation at a theoretical rate of 32 strokes per min. The control of the pump is through regulation of the time of exhaust of air from the driving member, and this valve also acts as a complete shutoff for the pump. The valve, as presently constructed, permits pump operation from 1 stroke per min to about 100 strokes per min. However,

the maximum quantity of liquid oxygen which the pump will handle depends upon the degree of perfection and control of the loading of the cylinder. The pump has been operated up to 250 strokes per min. If satisfactory loading characteristics could be maintained at this rate of operation, some 200 lb of liquid oxygen per hr might be injected.[6]

6.6 HAND-OPERATED LIQUID OXYGEN PUMP

This apparatus was designed to provide a means of charging high-pressure (2,000 psi) oxygen cylinders from a source of liquid oxygen at atmospheric pressure. The apparatus is hand-operated and its heat requirements are supplied by the surrounding atmosphere.[3]

Liquid is compressed by a piston from atmospheric pressure to that required and is then led through an air-warmed vaporizer in which it is converted to compressed gaseous oxygen. The compressed gas is led through a gauge connection into the cylinder to be charged. By compressing liquid instead of gaseous oxygen, the work necessary for the operation is minimized.

The finished apparatus conformed to the following specifications:

1. Weight (empty) 140 lb
2. Height 33 in.
3. Space required 16 x 50 in.
4. Container capacity 21.5 lb
5. Pumping rate 10 scfm (average)
6. Losses
   a. Loss on filling (warm), 4.0 lb
   b. Loss on standing, 0.6 lb per hr
   c. Loss on pumping one filling of oxygen (200 cu ft delivery), 3 lb
   d. Limiting overall oxygen efficiency, 85%

The apparatus shown in Figure 22 and Figure 23 includes a vacuum vessel (Figure 23) provided with a filler port and a vent. In this vessel is a nitralloy cylinder with a close-fitting piston of the same material, which is actuated by the handle. The cylinder

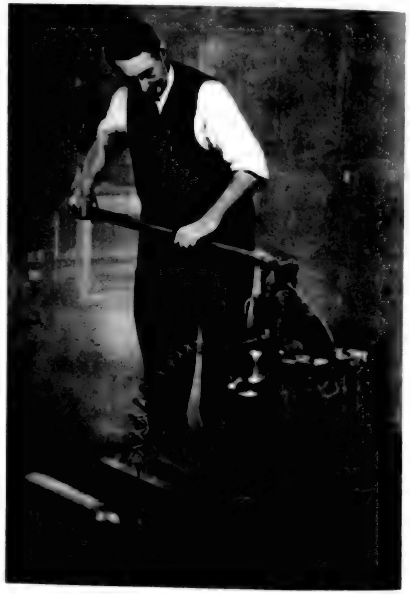


FIGURE 22. Hand-operated liquid oxygen pump.

is fitted with a ball check valve to prevent backflow of oxygen. The vaporizer is mounted on the pump frame in such a way as to allow free convection of air. The oxygen outlet is provided with a gauge by means of which the cylinder pressure is read.

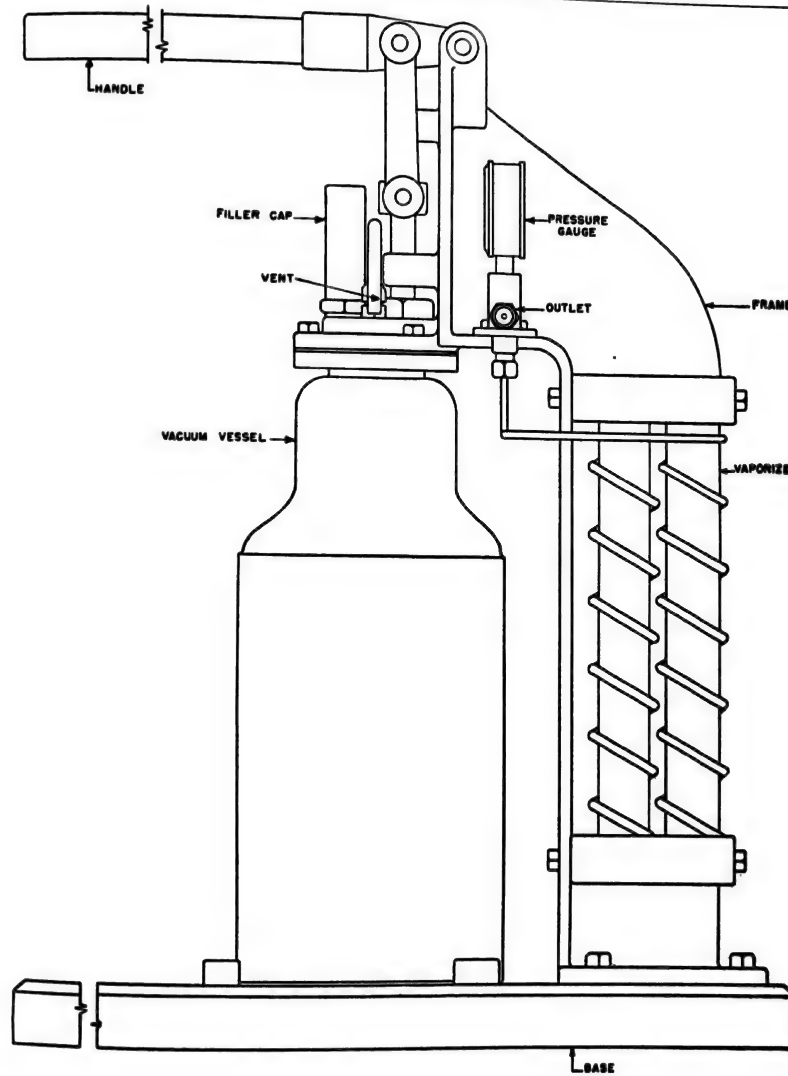


FIGURE 23. Hand-operated pump and vaporizer.

Chapter 7

HEAT EXCHANGE

By *J. H. Rushton*

7.1 COOLING ATMOSPHERIC AIR TO LOW TEMPERATURES

ONE OF THE most important pieces of equipment in any air liquefaction process is the heat exchanger. Regardless of the pressure under which the system operates or the type of refrigeration used, it is necessary to conserve such refrigeration in order to make the liquefaction of air economical or even possible. Two types of cycles, the low-pressure and the high-pressure, were considered for oxygen production for both the mobile oxygen units and the large liquid submarine units. It was necessary to produce the most compact heat exchanger consistent with the minimum pressure drop for the purpose of recovering the maximum amount of refrigeration from the effluent gases to the incoming air. A large part of the refrigeration load of an oxygen-producing unit can be wasted by large temperature differences at the warm end of the exchanger system. Most designs required temperature approaches at the warm end of the order of 4 to 6 F.

High-pressure heat exchangers of efficient design had been rather common in the industry and in experimental laboratories, but efficient and compact heat exchangers for low-pressure liquefaction units were not so well developed. Accordingly, a considerable amount of effort was expended to develop compact low-pressure heat exchangers.

The problem of the design of mobile oxygen plants for the Armed Forces led immediately to the thought that low-pressure plants were particularly suitable for the purpose.[6] Because of the low operating pressure, the heat exchangers themselves may be used to remove water and carbon dioxide from the air going to the fractionating equipment. Thus, there may be eliminated the usual bulky and heavy air dryers and carbon dioxide absorbers, freeing the unit of chemical supply problems. Another advantage of a low-pressure system is that the power requirement, and therefore the size of the driver engine and necessary gasoline supply, is at a minimum. Low operating pressures also make possible the use of rotary compressors and expanders with a consequent saving in weight and size of equipment.

Important elimination of a continuous supply of alumina or silica and caustic soda or potash is achieved by removing water and carbon dioxide from the refrigerated air in the main exchanger. This is accomplished by alternating periodically the flows between the two passages. A half-cycle time of three minutes is usual[6] and in this way, while air is being cooled during one half of the cycle, water and carbon dioxide are condensed out of the air and accumulated on the exchanger surface. Before the accumulation has become large enough to cause plugging of the exchanger, the two streams are interchanged and low-pressure nitrogen flows over the accumulated deposits and evaporates them while the air deposits its impurities in either another exchanger or on the other side of the heat exchanger surface. The evaporation is influenced by two factors: the pressure differential between the two streams, which aids evaporation; and the temperature differential, which hinders it. Continued operation of such exchangers, and the removal of condensable impurities, are only possible when these two factors are in proper balance.

The oldest and most successful exchanger operating in this manner is the regenerator system used in the Linde-Fränkl plant.[6] In this case there are two sets of regenerators, which are cylindrical vessels filled with disks of crimped aluminum ribbon coiled tightly in the form of a spiral. High-pressure air flows through two vessels, while low-pressure nitrogen and the oxygen product flow through the other two, the flows being reversed periodically from one set of regenerators to the other. The transfer of heat between the two streams depends upon the storage of heat or refrigeration in the metal packing during each phase of the cycle. The two gases are never in direct thermal contact across a metal surface. The cycle time in regenerators affects the heat transfer efficiency, as well as the thickness of the deposits formed and laid down during each phase of the cycle.

Regenerators of this type have been used in the Linde-Fränkl plants in Germany where long-time operation is desired. However, as there were little or no design data available on this type of equipment,

a study for the determination of regenerator performance was carried out.[7,8] Before the data from the research were available it was necessary to set the size of such equipment for the first mobile unit, known as M-2. The results obtained later indicated that it would be advisable to increase the size of these units, and this was done by adding another section to each unit.

The main differences between the regenerators set for the M-2 unit and the Linde-Fränkl ones lay in three points:

1. The M-2 regenerators were smaller than any of those known to have been built.
2. The M-2 regenerators were designed for a greater temperature difference at the warm end, in order to decrease weight and size.
3. The M-2 system did not use a small percentage of purified high-pressure air which gave the unbalanced flow used in the Linde-Fränkl plants.

Collins had devised a low-pressure heat exchanger for a small oxygen unit (see Chapter 3) which showed great promise of providing the desired type. The Collins exchanger[2,3,6,10] consists of annular sections filled with spirally wound ribbon. This is illustrated in Figure 1. In addition to its excellence as a heat-exchanger device, this machine was also capable of operating as an air purifier by removing water and carbon dioxide and light hydrocarbons by condensing them in the stream of incoming air. These impurities could then be evaporated when effluent gas streams were passed countercurrently through the same passages, and thus the exchanger could be used in a reversing fashion; these exchangers are normally referred to as *reversing heat exchangers*.

Reversing exchangers consisting of these Collins tubes are characterized by a high rate of heat transfer and a small total surface, as compared with regenerators which operate with low heat transfer rates and large surfaces. The thermal efficiency of a Collins tube exchanger is less affected by cycle time than are regenerators because there is essentially no storage of heat in the metal.

T[illegible] condition that each passage of a regenerator or [illegible]ersing exchanger be capable of carrying the low [illegible]essure gas with a reasonably low-pressure drop re[illegible]s that both passages be rather large. For this re[illegible] this type of exchanger is limited to low pressu[illegible]because, as the pressure goes up, the loss of co[illegible]ssed air on reversal finally becomes prohibiti[illegible]onstruction is also heavy, as advantage cannot be taken of the fact that the high-pressure air stream could be carried in relatively small conduits, due to the allowable pressure drop.

Other extended surface exchangers were used for various applications and will be referred to in due course.

High-pressure exchangers, for the most part, have been designed using suitable tubing both in parallel straight passes and spirally wound passes. One of the most successful high-pressure exchangers was that incorporated in the Giauque unit (Chapter 4), and which is referred to as the Giauque-Hampson exchanger.[14,15] This exchanger is illustrated in Figure 9. The Giauque-Hampson type exchanger was also used to purify incoming air by means of refrigeration. However, when acting as purifiers, these exchangers were allowed to have impurities deposited and, before any serious pressure drop or blocking occurred, were then switched out of the line and thawed to such a temperature that the impurities could be drawn off as liquid or blown out as vapor. Heat exchangers used in this fashion are referred to as *switch exchangers*.

Although the first small mobile unit M-2 was built with Fränkl-type regenerators,[1] the results obtained by Collins indicated that a saving in weight, volume, and loss of high-pressure air could be obtained by the substitution of reversing exchangers for the regenerators. Since the oxygen produced had to be highly compressed before use, it had to be free of oil and, therefore, could not be warmed in a regenerator which had previously been contaminated by air carrying oil. The Collins tube, on the other hand, can be built with a third annulus or tube in thermal contact with the two annuli which carry air and nitrogen alternately. This can be used to carry the oxygen stream continuously. Thus, since the oxygen-warming surface is never in direct contact with air, the oxygen discharged from Collins tubes will be free of oil and very dry. Again, due to the smaller size, there is less loss of high-pressure air on reversal and depressuring with the Collins tube exchangers. As the original 1⅝-in. OD tube designed and tested by Collins was small, and thus required a large number to be used in parallel in a unit to produce 1,000 cfh of oxygen, a larger-diameter tube was developed. Such a section of 3¼-in. OD was built and tested for heat transfer with excellent results. Consequently, when the M-2 unit on the first run failed to produce liquid, due to poor insulation and excessive heat leak, it appeared advantageous

to switch to the larger tubes on this unit, later to be called M-2R, as well as on the M-7, or single-trailer unit. The latter was made possible by the great reduction in space requirement obtained by the use of the Collins exchangers.

In the Linde-Fränkl plant, as mentioned above, a small portion of the air taken into the plant is dried and freed of carbon dioxide, and is used to unbalance the flows in the regenerators, making the low-pressure stream somewhat larger than the high-pressure stream. This has been reported to be necessary in order to insure complete removal of impurities from the regenerators over a long period of time. Early tests made with reversing exchangers by Collins indicated, however, that successful operation was possible with balanced flow, and that reversing exchangers differed from regenerators sufficiently to make unbalancing and consequent purification of a portion of the air unnecessary. The reversing exchangers in the mobile units were designed to operate with balanced flows which resulted in the simplification of equipment desirable in a mobile unit.

7.2 HEAT EXCHANGER FOR LOW-PRESSURE OPERATIONS

The use of Collins exchangers in air liquefaction plants is a recent development which promised to be of considerable importance. These exchangers are essentially concentric tubes joined by a coiled ribbon packing metallically bonded to the tubes. They were successfully applied by NDRC contractors to both small and large units for the production of gaseous oxygen by liquid air fractionation. The Collins unit has a capacity of 150 scfh (standard conditions of 60 F and 1 atm) at 99.5% purity; the units known as M-2R and M-7 each have a capacity of 1,200 scfh oxygen at 99.5%; M-3 has a capacity of 325 scfh at the same purity, and M-5 a capacity equivalent to 400 lb liquid oxygen per hr. The Collins unit operates at a head pressure of 150 psi, while the latter four units operate on an air pressure of 105 psia.

The Collins type exchangers serve a two-fold purpose, namely, recovery of refrigeration, and removal of condensable impurities such as water and carbon dioxide.[1,6] To effect removal of impurities the inlet high-pressure air and the returning nitrogen-rich waste gas alternate with each other in flowing through their two-heat transfer channels, each gas always flowing in the same direction through either channel. The impurities deposited by the high-pressure air are picked up after "reversal" by the waste gas and carried back to the atmosphere. Reversals occur at frequent intervals and are automatically controlled.

7.3 HEAT TRANSFER RATES IN COLLINS EXCHANGER PACKING

This section presents a correlation of heat transfer data in Collins exchanger tubes, which has served as a satisfactory design criterion.[5] The recommended correlation applies to all the various types of Collins packing used in the program.

Data on the 1⅝-in. OD double-annulus tube were obtained by Collins of the Massachusetts Institute of Technology before March 1942,[10] and on the 3¼-in. OD double-annulus tube by Dodge of Yale University in 1942.[9]

The exchangers are concentric tubes with coiled ribbon packing in the space between tubes. This packing is made by winding a copper ribbon on edge on a mandrel and then stretching the tightly wound coil to form a helix of desired pitch. The coil is wound upon the smaller of the two tubes bounding the annular space, and adjacent turns are separated by solder wire. The outer tube is slipped over the packing; good mechanical contact between packing and both tubes is made either by expanding the inner tube or contracting the outer, and the assembly is heated to form a solder joint between the packing and the tubes.

Figure 1 shows the dimensions of the tubes and packing used in the test exchangers. The 1⅝-in. OD exchanger has a 7-ft effective length; the other, 19.5 in.

The 1⅝-in. exchanger tube tested at MIT was suspended in a chamber evacuated by a diffusion pump. To reduce radiation the exchanger was wrapped with aluminum foil. The nitrogen or helium gas circulating in a closed system entered the inner annulus at approximately 90 psia and room temperature. Gas leaving the other end of the exchanger was throttled to about 20 psia, cooled against liquid nitrogen, and returned through the outer annulus. A bleeder line was installed between the exchanger and the throttle valve.

Tests on the 3¼-in. OD exchanger were conducted at Yale. Compressed air at room temperature passed through the outer annulus, was heated

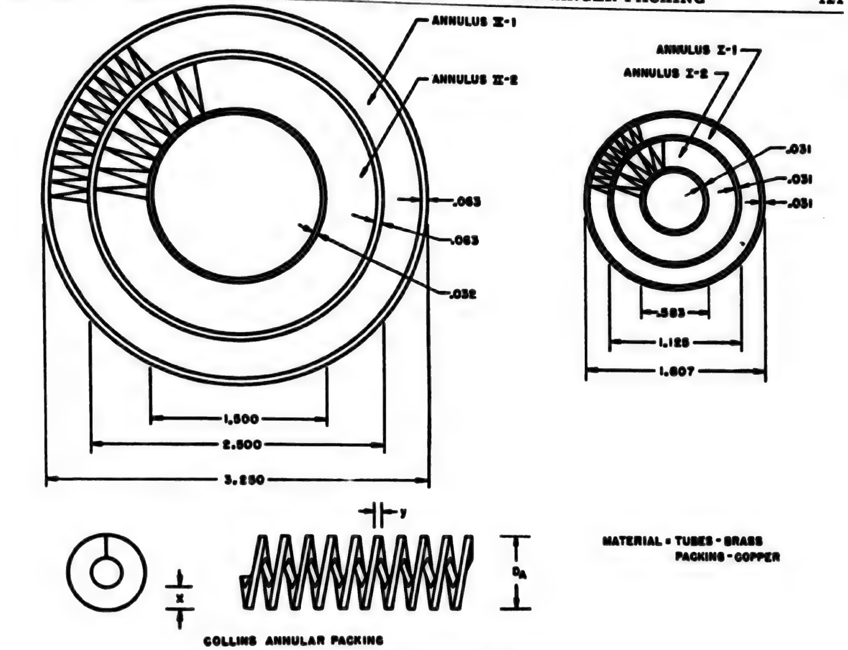


FIGURE 1. Collins exchanger tube details.

to approximately 200 F in a steam heater, and returned through the inner annulus. Before being released to the atmosphere the air flowed through a displacement-type gas meter. The four terminal temperatures were measured by copper-constantan couples. The tube and the headers were insulated with magnesia.

The following equation correlates the performance:

$$\frac{h_f D_e}{k} = 0.114 \left(\frac{D_e G}{\mu}\right)^{0.7} \left(\frac{C_p \mu}{k}\right)^{1/3} \quad (1)$$

h_f = fluid film coefficient, applied to entire wetted surface, Btu hr^{-1} ft^{-2} F^{-1}.

D_e = equivalent diameter, feet, and is defined as $4S/b$ where S = volume occupied by fluid per ft of tube length, ft^3 per ft, and b = total wetted surface (tube plus ribbon) per ft of tube length, ft^2 per ft.

G = mass velocity of fluid, lb hr^{-1} ft^{-2} = W/S.

W = rate of fluid flow, lb per hr.

k = thermal conductivity of fluid, Btu hr^{-1} ft^{-2} (F per ft)$^{-1}$.

μ = viscosity of fluid, lb hr^{-1} ft^{-1} = 2.42 × centipoises.

C_p = specific heat of fluid at constant pressure, Btu/lb.

This equation fits the data with an average deviation of 2.5% and a maximum of 5.8%.

The sixteen test runs cover the following range of variables:

h_f	26.8 to 90.3
D_e	0.00722 to 0.00999
μ	0.327 to 0.0491
k	0.0106 to 0.0718
$D_e G/\mu$	393 to 6800
$C_p \mu/k$	0.69 to 0.78
Fluids	air, nitrogen, helium

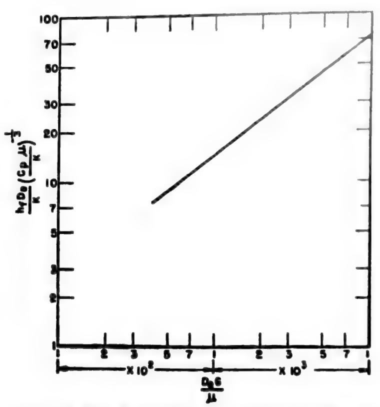


FIGURE 2. Plot of equation for heat transfer in Collins packing.

Fluid properties should be evaluated at mean fluid temperature. To calculate the overall coefficient U_r based on any reference surface b_r, the following general equations are used:

$$\frac{1}{U_r}=\left(\frac{1}{h_{f1'}}+F_1\right)\frac{b_r}{b_1}+\left(\frac{1}{h_{f2'}}+F_2\right)\frac{b_r}{b_2}+\frac{t_w}{k_w}\frac{b_r}{b_w} \quad (2)$$

$$h_{f'} = h_f \times \text{fin efficiency} \quad (3)$$

where U_r = overall coefficient based on surface b_r, Btu hr^{-1} ft^{-2} F^{-1}.

b_r = arbitrary reference surface, ft² per foot of exchanger length.

F = fouling resistance, Btu^{-1} hr ft² F, corrected for fin efficiency.

t_w = thickness of wall between the two fluids, ft.

k_w = conductivity of wall material, Btu hr^{-1} ft^{-2} (F per ft)$^{-1}$.

b_w = mean of inner and outer wall surfaces, ft² per ft of exchanger length.

Subscripts 1 and 2 refer to the two fluids between which heat is being exchanged.

The fin efficiency may be [illegible] ing that the fins are straight [illegible] section extending from [illegible]

When the [illegible] formance is [illegible]

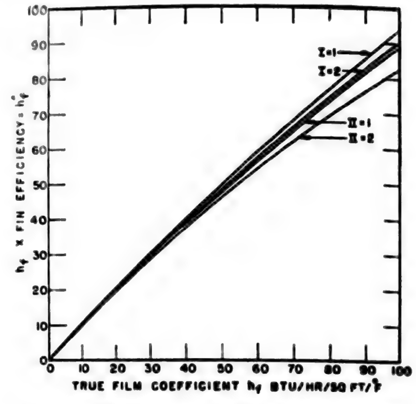


FIGURE 3. Fin effectiveness of Collins exchanger packing.

where Q is the heat transferred, Btu per hr, ΔT is the mean temperature difference between the two fluids, F, and A_r is the reference area, sq ft, calculated as the product of b_r and the effective length of tube in the exchanger.

7.4 RECTANGULAR MULTIPIN HEAT EXCHANGER

The reversing heat exchangers prove to be very successful both for heat exchange and air purification.[13] However, their configuration was such that it was necessary to manifold a number of tubes in parallel even for small-sized plants. The large M-5 liquid oxygen unit (see Chapter 3) had originally been laid out using regenerators and one of the original requirements for the plant was that it need operate continuously for a period of only 10 to 12 hr at low-temperature producing conditions. After the successful temperatures of the reversing heat exchanger technique, it was felt desirable to re-engineer the M-5 unit so as to make it capable of operating continuously for days or weeks at a time, if desired. The regenerator system originally installed was not capable of such continuous operation. A large-sized [illegible] was laid out on the basis of using Collins [illegible] (60 in parallel) for the heat exchanger system [illegible] M-5 unit, and these tubes have operated su[illegible]. However, it had long been felt that the [illegible] a considerable saving both in expense [illegible]

fabrication of Collins heat exchangers and in space and heat insulation losses if an exchanger could be devised which would allow larger individual flow passes for the gases. Such an exchanger was finally built in size sufficient for a 1,000 cfh gaseous oxygen unit. This exchanger was then the equivalent of the exchanger system in the M-7 units. The actual cross-section area for the same performance as for the Collins tubes was between 40 to 50% of that required for the Collins tubes. Manifolding was considerably simplified in this exchanger which is shown in Figure 4. The final design of the exchanger has been named "Multipin" (Figure 5), and is so referred to in reports.[15]

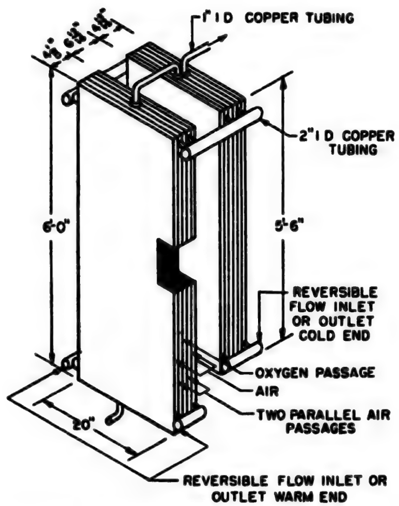


FIGURE 4. Rectangular exchanger for pilot plant tests.

The exchangers are parallel plates with a rectangular coil-wire packing in between them. The packing is made by winding copper wire in the form of a rectangular helix of desired pitch, height and width. Helices are wound right- and left-handed alternately in order that they may mesh together. The meshed helices form the packing which is placed between solder sheets and then between copper plates to form the separate channels of the exchanger. The assembly is heated to form a solder bond between the packing and the plates. In this process the ends of the rectangle contacting the channel plates are covered with solder so that each exchanger passage becomes in effect two parallel plates connected by a multitude of straight pins.

Basic dimensions of the packing and exchanger are listed below.

Wire diameter	0.032 in.
Packing	0.760 in.
Pins per square inch packing	248
Solder sheet at contact surface, thickness	0.020 in.
Copper passage plates, thickness	0.043 in.
Exchanger passage, width	20.0
Exchanger passage, length	11 ft 6 in.

The exchanger was built in two sections in series, one 6 ft and the other 5 ft 6 in. long with the shorter

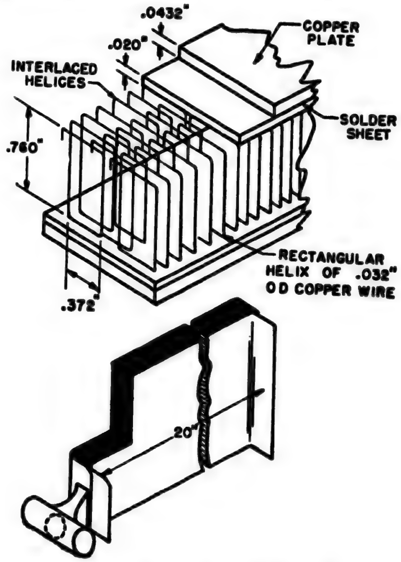


FIGURE 5. Details of basic Multipin section.

length at the colder section of the exchanger. The warm section of the exchanger thus contained 5 passages and the cold section was built with 6 passages. Exchanger details are shown in Figure 5.

The Multipin exchanger occupies 1.46 cu ft, or slightly less than half the volume of a Collins tube assembly. Actually the comparison is even somewhat more in favor of the Multipin exchanger because the

controlling pressure drop through the Collins assembly would be approximately 4.5 psi as against a pressure drop of some 3 psi for the former exchanger. A Collins exchanger, to do the same heat transfer duty at the same pressure drop found for the Multipin exchanger, would have to be somewhat larger than estimated in the preceding paragraph, and increase further the volumetric saving afforded by the Multipin assembly.

A clear comparison between the characteristics of the two exchangers required to perform the duty being discussed can be obtained from the following table.[15]

Exchanger	Volume, ft^3	Effective Area, ft^2	Pressure Drop, psi
Multipin	1.46	378	3.0
Collins	3.06	470	4.5

Another advantage of the Multipin construction lies in the relatively easier manifolding problem, with consequent reduction in volume of manifold piping required per volume of exchanger.

It is interesting to note that the gas film coefficient can be predicted and good agreement made with the experimental results obtained through the use of a simplified dimensional equation for gases flowing normal to staggered tubes. This equation is

$$h = 0.133 c_p G_{\max}^{0.6} D_0^{0.4} \tag{5}$$

where $G_{\max} = W/S$

D_0 = outside tube diameter, ft.

Application of this equation directly to this case results in a value of $h = 62.3$ which is twice the figure observed. This is at least partly explainable since the Multipin exchanger utilizes pins which are soldered to the passage walls and this wall effect is not considered in the above equation.

However, if the above equation is modified for the present conditions by substituting D_e for the pin diameter and thus basing the coefficient on total washed surface the predicted coefficient is,

$$h = \frac{(0.133)(0.24)(182)}{(0.1575)} = 36.9. \tag{6}$$

The observed coefficient, corrected for fin efficiency is

$$h_{\text{observed}} = \frac{30.2}{0.823} = 36.7$$

The agreement is surprisingly excellent and, although this may be coincidence, it is worth notice in passing, and if more experimental data becomes available, warrants further investigation.

There is strong evidence that the increased heat transfer performance obtained in the Multipin exchanger is the result of added fluid turbulence in the packing. As indicative of the magnitude of this effect it is estimated that the friction factor obtaining at a value of modified Reynolds number of 1,500 in the clean exchanger is approximately 0.35. The value of the friction factor for the same Reynolds number in a Collins tube would average 0.13, although this figure might be as high as 0.15 for certain samples.

The equation (1) for predicting the heat transfer coefficients in Collins tubes has been applied to the Multipin exchanger and found to be very conservative. The experimental data available indicate a value of h approximately 75% greater than that predicted by the present equation. Since the experimental data are very meager it is recommended that the equation for Collins tubes be retained in form for the Multipin exchanger with a 50% increase in the constant of the equation. This equation then becomes

$$\frac{h_f D_e}{K} = 0.175 \left(\frac{D_e G}{\mu}\right)^{0.7} \frac{c\mu^{1/3}}{(K)} \tag{7}$$

It is further suggested that the simplified dimensional equation

$$h_f = \frac{0.133 c_p G^{0.6}}{D_e^{0.4}} \tag{8}$$

is equally applicable to this type of exchanger and should be checked if further experimental results become available.

A large-sized heat exchanger based upon this rectangular and multiple principle has been designed for incorporation in the M-5 liquid oxygen plant.[15] This work was carried on by the University of Pennsylvania Thermodynamics Research Laboratory under contract NObs-2477, and the continuation of this development can be followed by reference to reports from that laboratory under the Navy contract.

7.5 LIQUEFIER AND SUBCOOLER

A special exchanger sample was submitted by the Trane Company and its heat transfer and pressure drop characteristics determined in tests conducted at the Central Engineering Laboratory. This type of exchanger is to be used for the new liquefier and subcooler for units of the M-5 and M-6 type.[6,15]

The exchanger is a double-annulus packed tube 5 in. OD x 4 ft effective length, in which the annuli are packed with 0.013 in. thick corrugated sheet forming longitudinal fins about ⅛ in. apart and 0.680 in. high. The total wetted surface in the outer annulus is 50.9 sq ft and in the inner annulus 33.8 sq ft. Exchanger details are shown in Figure 6; Figure 7 shows the header construction.

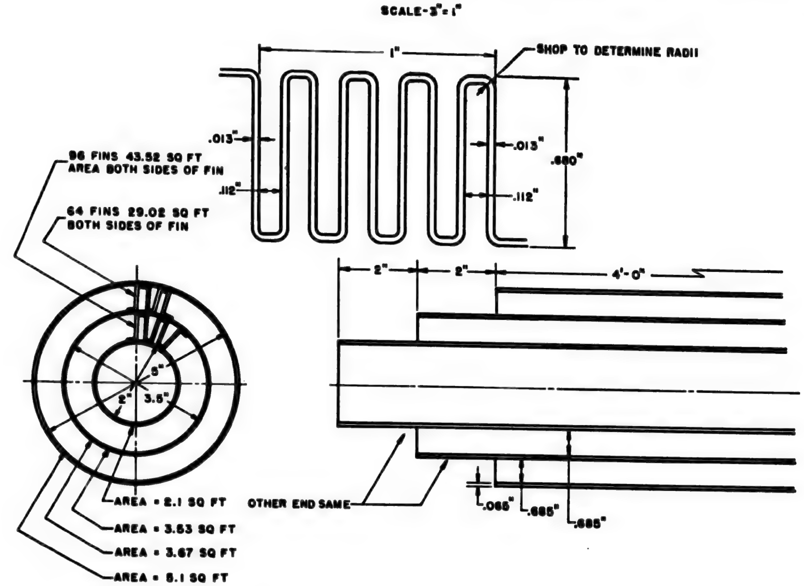


FIGURE 6. Trane exchanger and liquefier.

The exchanger was tested with air flowing through the inner annulus, then through a heater, and returning through the outer annulus. The air flow rate, terminal temperatures and pressures were measured. Additional pressure taps at the packing boundaries in the outer annulus permitted study of the pressure drop in the headers. The experimental data are summarized and the results plotted in Figure 8.

Predicted values of film coefficient were obtained using the Dittus-Boelter equation with D taken as the hydraulic diameter. Correction for fin efficiency was then made for each annulus using the method of McAdams. Because of unexplained discrepancies in temperature measurements the test results were calculated in two ways. Terminal temperatures were first taken as the average between glass thermometer and thermocouple readings, and then from the glass thermometer readings alone. The experimental results are shown as crosses. The experimental points fall well below the predicted values. The curve through the experimental points is obtained by including a fin contact resistance in addition to the fin efficiency already considered. The value of this contact conductance (inverse resistance) required to correlate the experimental data is 320 Btu per hr per sq ft per F. This is a total figure for both annuli and is based on the 3.5 in. tube surface.

Pressure drop characteristics were treated very briefly for the outer annulus only, since no header pressure drop correction was available for the inner annulus. The friction factor was found to be some 30 to 40% higher than predicted by standard methods.

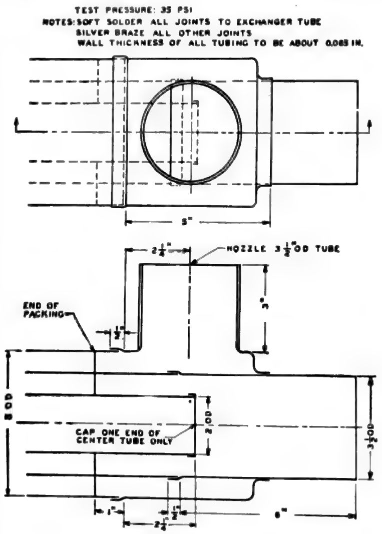


FIGURE 7. Trane exchanger header details.

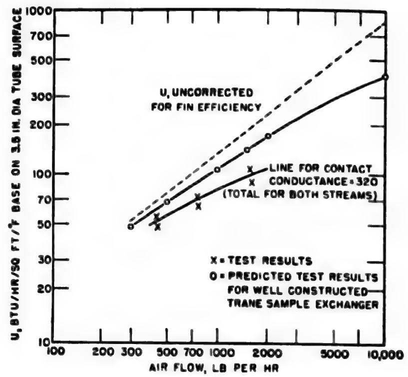


FIGURE 8. Heat transfer correlations for Trane exchanger.

7.6 HIGH-PRESSURE HEAT EXCHANGERS

The use of Hampson-type exchangers in gas liquefaction plants has long been practiced. This type of heat exchanger, first devised by Hampson, consists of coils of small high-pressure tubing wound spirally within a cylindrical shell. In general, the entering high-pressure process gas is carried in the coils, which are washed by cold low-pressure waste gas. This form of exchanger is very efficient and compact, and has been successfully used in this program in several small units for the production of oxygen by liquefaction and fractionation of air.

Although in general use for many years, no data were available for the accurate design of such exchangers until the results of W. F. Giauque's experiments at the University of California were obtained.[14] The exchangers were built and studied by Giauque in connection with the development of a liquid oxygen generator, and are essentially modified Hampson exchangers consisting of tubing wound in helical layers within a cylindrical shell. The tubes are built up layer by layer with alternate layers wound left and right. By selecting the proper number of tubes to be wound in parallel in a given layer, or by arranging crossovers between layers, all the tubes in parallel can be made of equal length. This basic design is used with various tube sizes and spacings to meet a variety of exchanger requirements. A detailed discussion of construction as well as test data is presented in a final report.[14]

7.7 HEAT TRANSFER COEFFICIENTS FOR HIGH-PRESSURE AIR INSIDE TUBES

Data on the individual heat transfer coefficients for high-pressure gas in small tubes were not available prior to the work of Giauque. The experimental results were correlated by Giauque through the use of a modified dimensional equation used for low-pressure gases flowing inside tubes. However, it seemed desirable to correlate the results more generally by the use of a proven dimensionless equation and in this way, if possible, extend the application of a standard and common method of predicting the heat transfer coefficient to this case.

Four copper tubes 0.250-in. OD (0.035-in. wall) were soldered together in parallel for a length of 40.5 ft to form the exchanger, two tubes being used for each passage.[14] Terminal temperatures and pressures were measured in a series of four experiments at various elevated pressures in which air was taken through two of the tubes, passed through a cooler and then passed counter-current through the two remaining tubes. The exchanger was made in the form of a loose coil about 20 in. in diameter and well insulated. Calculations were made for each third of the exchanger length, and heat leak and metal resistance were assumed to be negligible. The air flow was 1.43×10^6 lb per hr per sq ft and a summary of calculated results is given in Table 1.

TABLE 1. Summary of experimental results. Individual heat transfer coefficients for high-pressure air inside ¼ in. tubing.

Run No.	Average pressure (psia)	Average temp. (F)	h, heat transfer coeff Btu/(hr)(sq ft)(F)
1a	3,260	+ 12.5	813
2a	2,420	+ 9.0	801
3a	1,540	+ 6.9	711
4a	3,550	+ 15.9	788
1b	3,260	− 50.0	864
2b	2,420	− 54.0	822
3b	1,540	− 56.7	762
4b	3,550	− 47.6	826
1c	3,260	−103.	997
2c	2,420	−105.	975
3c	1,540	−110.	926
4c	3,550	−103.	940

Correlations. The results of Table 1 were correlated by Giauque using a modification of the simplified dimensional equation

$$h = 0.0144 c_p G^{0.8} D^{-0.2},$$

where h = Btu/(hr)(sq ft)(°F),
c_p = specific heat, fluid, Btu/(lb)(°F), (9)
G = fluid flow, lb/(hr)(sq ft),
D = ID tube, ft.

The correlation was satisfactory when the constant of equation (9) was reduced to 0.0120, the equation becoming:

$$h = 0.0120 c_p G^{0.8} D^{-0.2}. \qquad (10)$$

It is not surprising that the constant of equation (9) was found inapplicable since this equation is a simplified form of the general Dittus-Boelter expression

$$\frac{hD}{k} = 0.023 \left(\frac{DG}{\mu}\right)^{0.8} \left(\frac{c_p\mu}{k}\right)^{1/3}. \qquad (11)$$

where all terms are the same as previously defined with the addition of:

k = thermal conductivity of fluid Btu/(hr)(sq ft)(F per ft)
μ = fluid viscosity, lb/(hr)(ft)

Equation (9) is derived from expression (11) by inserting average values of:

$$\frac{c_p\mu}{k} = 0.78$$

and $\mu = 0.0435$

Since the values assigned above do not hold at the extreme temperatures and pressures existing at the conditions of test, it is easy to understand the need for an adjusted constant to correlate the experimental results by means of simplified equation.

It was felt that in light of the deviation of the test results from equation (9), it might be better to correlate the data using the dimensionless Dittus-Boelter relation to compensate for the variation in the thermal properties of the fluid over the temperature and pressure ranges covered. The only drawback to this approach is the necessity for extrapolating existing data for the fluid properties to evaluate these properties at the experimental conditions. However, the extrapolation was not too difficult and it was felt that such an estimate was superior to the assumption that the physical properties of air remained constant over the range of interest.

A summary of the heat transfer coefficients predicted by the Dittus-Boelter equation for the conditions existing in the 12 experimental runs reported in Table 1 is given in Table 2. The physical properties of air were all taken from the Data book, Report OSRD Number 4206, with the exception that values of c_p not included in this report were taken from the data of Williams.[11] Values of viscosity and the group $c_p\mu/k$ are tabulated to indicate the extent of the deviations in these values from the average figures assumed in equation (9).

F. G. Keyes[11] has also analyzed the data of Giauque using the Dittus-Boelter equation and somewhat different relations for determining air properties. The calculations of Giauque and Spector[15] are compared with the observed experimental results in Table 3.

Heat Transfer in Coils. Consideration of the effect upon the heat transfer coefficient resulting from the use of high-pressure tubes wound in helical layers led to the investigation of the individual heat transfer coefficients in 3/16-in. tubing coiled in a spiral of very small diameter. Experimental procedure similar to that described in the previous section was adopted using an exchanger wound in a spiral ⅝-in. ID. For this severe case the value of the heat transfer coeffi-

cient was found to be increased approximately 30% of that for larger diameter coils. Since the diameter of the coils used in most Hampson-type exchangers is considerably larger than the test spiral, it is estimated that the increase in heat transfer coefficient due to coiling, is very small for the cases of interest.

Recommendations.[15] In order to avoid the necessity for using special correlations in the design of Giauque-Hampson exchangers it is recommended that the value of the heat transfer coefficient inside the tubes be calculated from the Dittus-Boelter relation, equation (11), those predicted by the Dittus-Boelter relation is excellent until an average operating temperature in the neighborhood of —100 F is reached, where the use of this equation results in values which are conservative by as much as 15 to 25%. Since the air properties used at this temperature have been estimated by extrapolation of unknown quality, it is suggested that the use of more accurate physical data might result in better agreement for such cases; and it is recommended that this point be checked if and when more accurate data on the physical properties of air become available.

TABLE 2. Predicted heat transfer coefficients for high-pressure air inside ¼-in. tubing. Dittus-Boelter equation.

Run No.	Pressure psia	Temp. F	Viscosity lb/(hr)(ft)	$c_p\mu/k$ dimensionless	h, Btu/(hr)(sq ft)(F)
1a	3,260	+ 12.5	0.0590	1.03	821
2a	2,420	+ 9.0	0.0542	1.01	805
3a	1,540	+ 6.9	0.0490	0.95	765
4a	3,550	+ 15.9	0.0600	1.05	825
1b	3,260	— 50.0	0.0546	1.16	910
2b	2,420	— 54.0	0.0499	1.12	804
3b	1,540	— 56.7	0.0450	1.06	760
4b	3,550	— 47.6	0.0579	1.21	830
1c	3,260	—103	0.0508	1.32	862
2c	2,420	—105	0.0474	1.43	830
3c	1,540	—110	0.0410	1.39	700
4c	3,550	—103	0.0523	1.29	852

TABLE 3. Heat transfer coefficients for high-pressure air inside small tubes.

Run No.	h, Btu/(hr)(sq ft)(F)				% Deviation Table 2 calculations from observed
	Giauque eq (9)	Keyes eq (11)	Spector Table 2	Giauque observed	
1a	803	820	821	813	1.0
2a	790	815	805	801	0.5
3a	734	775	765	711	7.6
4a	815	767	825	788	4.2
1b	898	850	910	864	5.3
2b	863	844	804	822	2.2
3b	801	805	760	762	0.3
4b	900	955	830	826	0.5
1c	1,020	931	862	997	13.5
2c	1,056	917	830	975	14.7
3c	1,020	869	700	926	24.3
4c	996	932	852	940	9.4

This equation has been shown to check the results of Giauque's experimental work with sufficient accuracy for design purposes. This is especially true since the resistance to heat transfer inside the tubes is small compared with the resistance outside the tubes and is therefore not too important in the overall design of the exchanger.

The agreement between observed coefficients and

7.7.1 Heat Transfer Coefficients for Low-Pressure Air Outside Tubes

The previous section indicates that the controlling resistance to heat transfer in a Giauque-Hampson exchanger (Figure 9) lies in the low-pressure gas film outside the coils. Thus, the intelligent design of such an exchanger requires that the heat transfer coefficient for low-pressure gas flowing past the tube coils be capable of prediction with good accuracy. Furthermore, the correlation should be broad enough to include such variables of design as tube size, spacing between tubes (pitch), spacing between tube layers, and number of tube layers.

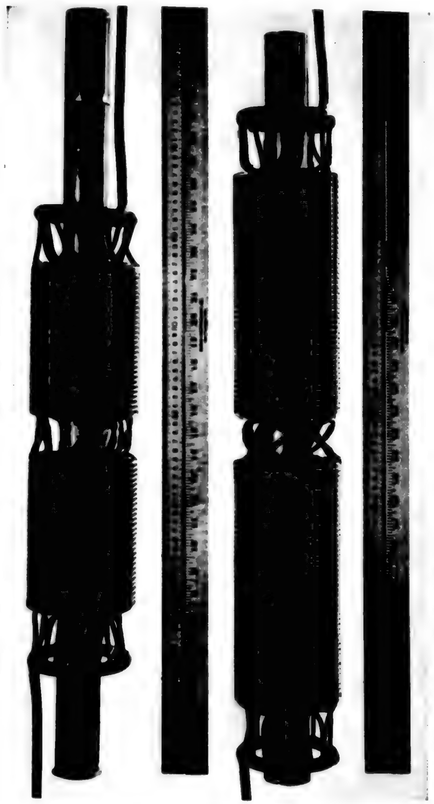


FIGURE 9. Giauque-Hampson interchangers, RLHL-3 (*left*) and RLHL-2 (*right*).

Five experimental exchangers of the same general type but embodying variations as noted above were built and tested.[5] No general correlation covering the performance of these exchangers was developed, but instead it was found necessary to express the heat transfer characteristics of each of the exchangers by the use of different equations.

Correlations. The results were correlated by Giauque using equations of the form,

$$h = Kc_p\left(\frac{W}{S}\right)^n \qquad (12)$$

where K = constant.
n = constant.
c_p = fluid specific heat, Btu/(lb)(F).
W = fluid flow, lb per hr.
S = superficial cross-sectional area of exchanger, sq ft (total area between inside of exchanger shell and outside of core tube).

Unfortunately this equation did not correlate all the data and different values of K and n were required by the data for each exchanger. Values of K ranged from 0.45 to 1.53 while n varied from 0.60 to 0.75.[14]

In considering a more general correlation the following variables were noted:

1. Tube size varied from ⅛ in. to ¼ in.,
2. Spacing between tubes (pitch) varied from 0.031 to 0.096 in.,
3. Spacing between tube layers varied from 0.000 in. to 0.053 in.,
4. Number of tube layers varied from 3 to 11.

In taking into account these variables the correction for tube size was made by a term D^a where D is OD of the tube in feet. Investigation of the literature on heat transfer to fluids outside of tubes disclosed no effect of pitch over wide ranges of this variable, and hence this factor was assumed to have no effect. The influence of both items 3 and 4 was included by the use of the term G^b_{max}, where G_{max} is pounds per hour of gas flow per square foot of net free cross-sectional area. This last assumption made it impossible to include exchanger RLHL-1 in the correlation, since the net free cross-sectional area available for gas flow could not be calculated with any degree of accuracy for this sole case where the spacing between tube layers was zero.

A literature survey disclosed that the value of the exponent a might well be taken as —0.4 and the value of b as 0.6 by analogy to heat transfer by fluids flowing outside banks of tubes. Accordingly the data were fitted to an equation of the form

$$h = K'c_pG^{0.6}_{max}D^{-0.4}. \qquad (13)$$

The calculations are summarized and the results plotted in Figure 10. The constants derived for each set of exchangers are:

Exchanger	K
RLHL-2	0.107
RLHL-3	0.102
RLHL-4	0.115
RLHL-5	0.115

The general equation correlating all the data is obtained from Figure 10.

$$h = 0.110 c_p G_{\max}^{0.6} D^{-0.4}. \qquad (14)$$

It is significant to compare equation (14) with the expression for gases flowing normal to staggered tubes which is given for the same units as

$$h = 0.133 c_p G^{0.6} D^{-0.4}. \qquad (15)$$

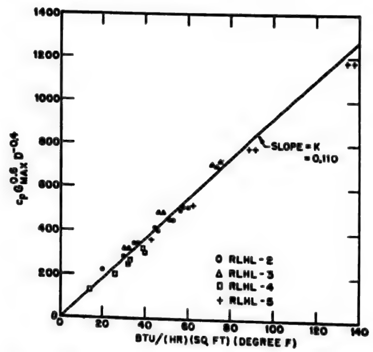


FIGURE 10. Plot of data on Giauque-Hampson exchangers.

7.8 RECOMMENDATIONS FOR HIGH-PRESSURE HEAT EXCHANGERS

Heat Transfer.[15] In the design of Giauque-Hampson exchangers it is recommended that the Dittus-Boelter equation be used to evaluate the heat transfer coefficient inside the tubes, and that the dimensional equations (14) and (15) apply to low-pressure gas flowing outside the tubes.

Use of these equations is desirable since neither expression is unique for this application. The Dittus-Boelter equation is generally applicable in cases of fluid flow inside tubes, and the above correlation for low pressure gas outside tubes agrees within 12% with a similar expression found to apply for the general case of gases flowing normal to staggered tubes.

Since it was not possible to include exchanger RLHL-1 in the correlation because the spacings between tube layers was zero, the question naturally arises as to the minimum spacing between tube layers for which the correlation holds. It is felt that there is no minimum value as such, but rather that the limitation is imposed by the accuracy with which the free area can be determined for purposes of evaluating $G_{\max}$.

The spacing between tube layers for the four exchangers used in the correlation are the following[14]:

Exchanger	K
RLHL-2	0.036 in.
RLHL-3	0.018 in.
RLHL-4	0.052 in.
RLHL-5	0.033 in.

It is probable that the correlation applies to the smallest spacing practically attainable in an exchanger of this type, provided sufficient physical data are available on the exchanger to permit accurate evaluation of $G_{\max}$.

It would be of interest to consider the coil of this type exchanger as a packing and attempt a correlation on the basis of an equivalent diameter D_e. The correlation might then be expressed in terms of a dimensionless equation of the general type.

$$\frac{hD}{k} = K''\left(\frac{D_e G}{\mu}\right)^x \left(\frac{c_p \mu}{k}\right)^y. \qquad (16)$$

where all terms are as previously defined with the addition of

K'' = constant of the equation.
D_e = equivalent diameter, ft $= 4S/b$.
S' = volume occupied by fluid per foot of exchanger length, cu ft per ft.
b = total wetted surface per ft of exchanger length, sq ft per ft.
w = mass velocity, lb per hr.
$G = W/S'$ lb per (hr)(sq ft)
x, y = exponents.

Pressure Drop. This question can be adequately considered for the present by using standard friction factors to evaluate pressure drop inside the tubes. The pressure drop outside the coils can be obtained in the following manner.

Giauque has presented the following relation for pressure drop in one of his experimental exchangers,[13]

$$P_1^2 - P_2^2 = 3.8 \times 10^{-8} T \mu^{0.2} N \left(\frac{W}{S}\right)^2, \qquad (17)$$

where P = pressure, psia.
T = temperature, K
N = length of exchanger, ft.
μ = viscosity, poises.
W = fluid flow, lb per hr.
S = superficial cross section of exchanger, ft² (as previously defined for heat transfer).

This equation was obtained over an experimental range of W/S = 1,000 to 4,500 and a temperature range of 200–300 K and can be simplified to the expression

$$\frac{\Delta P_G}{N} = 1.135 \times 10^{-8} \left(\frac{\mu}{\rho}\right)^{0.2} \left(\frac{W}{S}\right)^2, \qquad (18)$$

where all terms are those of equation (17) with the addition of

P_G = pressure drop, psia, Giauque.
μ = viscosity, centipoises.
ρ = fluid density, lb per cu ft.

Unfortunately, equation (17) is based on a superficial area S and is not considered generally applicable without modification. The ratio R of actual cross-sectional area filled, to superficial cross-sectional area for the experimental exchanger under consideration can be calculated as equal to 0.578, and for any other exchanger being considered this factor can be evaluated as

$$R = \frac{\pi D^2 n^2}{4}$$

where D = tube OD, in.
n = coil pitch, in.

This provides a basis for application of equation (17) to other exchangers, assuming

$$\frac{\Delta P_G}{\Delta P} = \left(\frac{v_G}{v}\right)^2 = \left(\frac{0.578}{R}\right)^2 \qquad (19)$$

where v equals the gas velocity and the G refers to the Giauque equation (17).

The procedure for calculating pressure drop consists then of solving equation (18) at design conditions to obtain P_G, and then substituting this value in equation (19) and solving for ΔP. This method has been tested in practice and found satisfactory.

It is recommended that a general method of calculating pressure drop outside tubes be developed for these exchangers. Use of an equivalent diameter D_e for the exchanger and a modified Reynolds number $D_e G/\mu$ where the terms are as defined for equation (16) might allow correlation of pressure drop characteristics in terms of the commonly used friction factors.

7.9 OTHER HEAT EXCHANGER DESIGNS

A great many novel heat exchangers have been proposed and built in connection with the oxygen program. A description of these can be found in reports[10,15] and from performance data reported on them. Modifications of common types of heat exchangers have been used for process air in the M-7[6,18], M-5[6,15], M-6[6,15,16] and details can be obtained in these references.

7.10 RADIATORS AND AIR-COOLERS

The compressors used in the mobile oxygen units all required interstage and aftercooling. This was effected by conducting the interstage and final pressure air to radiators or exchangers of conventional type. Designs were based for the most part on manufacturers' data[6] although in some cases data were obtained in NDRC experimental work for specially placed intercoolers.[2,3,13]

In a series of reports[11] a number of different types of high-pressure exchangers are described and some test data given. These exchangers have to do with the compact high-pressure liquid oxygen generators of Keyes and A. D. Little-Latham design.[11,17]

7.11 REGENERATORS

Heat exchangers are a basic part of any low-temperature process for the liquefaction and separation of air components. Where the size of a plant is of major importance a good deal of attention must be given to the design of the exchanger so that maximum efficiency on a volumetric basis is realized. In considering the design of oxygen plants to be fitted into very limited quarters the potentialities of the regenerative type of heat exchanger were recognized. Such an exchanger has a large heat transfer capacity on a volumetric basis coupled with a very low resistance. An additional feature of the regenerator, which added

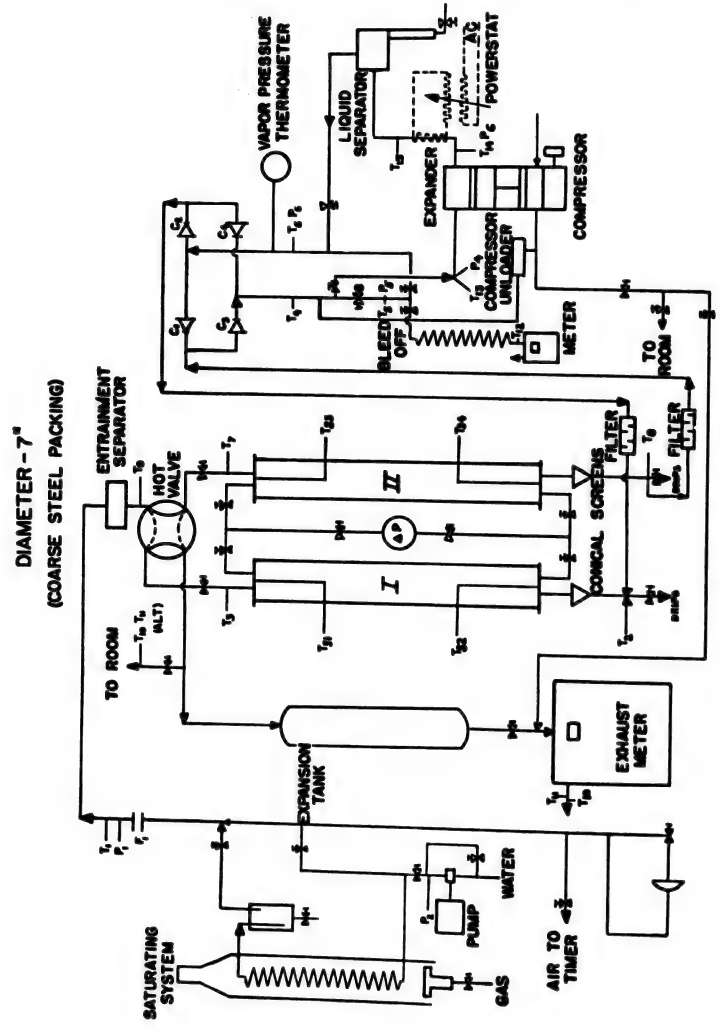


Figure 11. Typical flow sheet for regenerator tests.

to its attractiveness, is that removal of impurities from the process air is accomplished in the regenerator itself, eliminating the necessity of a preliminary cleanup system.

Although regenerators were employed in Germany in air liquefaction cycles, the amount of data available for use in the design of regenerator systems was very meager. To supply the need for such data an investigation was undertaken to determine the performance characteristics of several types of regenerator packings. These packings were patterned after those described in patents taken out by Fränkl in Germany. The object of the experimental tests was to evaluate the heat transfer and purification performance of the regenerators and determine the effects of various operating variables.

Five different types of packing were tested.[6,9] Each packing was made up of two parallel crimped ribbons with the direction of crimp at right angles to each other (see Figure 22, Chapter 8). These two crimped ribbons were wound into a close spiral to form pancakes of the desired diameter. The basic dimensions of the packings tested are given in the following table.

Table 4. Packing dimensions.

	3-in. aluminum	7-in. aluminum	7-in. fine steel	7-in. coarse steel	4½-in. copper
Height of crimp, in.	0.047	0.047	0.0218	0.047	0.0417
Pitch of crimp, in.	0.1275	0.1275	0.0625	0.1275	0.091
Thickness of strip, in.	0.013	0.013	0.013	0.013	0.015
Width of strip, in.	0.844	0.844	0.867	0.867	0.97
Per cent voids	67.8	70.0	55.7	69.1	61.9
Lb metal per cu ft	51	50	213	151	198

tory and a check valve assembly was substituted. The check valves (4) were arranged so that a flow reversal initiated at the warm end by the four-way valve was automatically completed at the cold end by the action of the check valves. The cycle controller used permitted variations in the time interval between flow reversals.

For the cold testing of the regenerators, two refrigeration procedures were used. In the first, air, after being cooled in the regenerator, was bubbled through liquid air and then returned to the particular regenerator which was being cooled. The amount of refrigeration used could be controlled by by-passing some of the air around the liquid air container. The use of liquid air as a refrigerant required the operation of a separate liquefaction plant and was costly and troublesome. It was later supplanted by an expansion engine. This expansion engine was a new development and gave some early mechanical trouble but in the long run proved a simple and easily controlled source of refrigeration.

The arrangement of the regenerators and auxiliaries is illustrated by the typical flow sheet of Figure 11. Table 5 presents a tabulation of some of the characteristics distinguishing the various test setups.[9]

The three essentials to the regenerator test setups were a compression system, a flow reversal system, and a refrigeration system. Two different types of standard compressors were used, and provisions were made to remove all entrained oil and water from the air to be processed. Scrubbing towers were also installed in conjunction with the compression system to permit removal of carbon dioxide from the air when that was desirable.

During the early tests on the regenerators flow reversal was accomplished by the simultaneous action of two four-way valves of the plug type, one at each end of the regenerators. The four-way valves were activated by an air operated plunger which in turn was operated by a cycle controller. Because of leakage and freezing, the use of a plug-type valve at the cold end of the regenerators was judged unsatisfac-

In making a test the inlet air pressure, temperature and humidity, the flow rate, the reversal time and cold end temperature level were set. Pressure control was provided by a pressure regulator and in most cases saturated air at a given temperature was supplied by a saturator system which included a water pump, gas-fired heater, and entrainment separator. The air passed through one regenerator and was then throttled into a distributor immersed in liquid air. The flow rate was controlled by this throttle valve. After passing through the liquid air, the air returned through the second regenerator and after passing through a surge drum was metered to the atmosphere. At intervals set for the given run the flow through the regenerators was reversed so that the regenerator, which gave up its cold to in-

coming air during one phase of the cycle, absorbed cold from the return air during the next phase of the cycle. This reversal was not only essential to the heat transfer performance of the regenerators, but also provided for purification of the process air by re-evaporating, on the low-pressure phase of the cycle, the water and carbon dioxide deposited out during the high-pressure phase.

after it had passed through the regenerator on high pressure.

The experimental data obtained in the course of the regenerator investigation are presented in summary form in a series of reports.[7,8,9] These data present a rather complete survey of the purification performance and the heat transfer and flow resistance characteristics of the particular packings studied.

TABLE 5. Essential differences of regenerator assemblies.

No.	Packing type	Insulation	Flow reversal	Refrigeration	CO_2 filter	Runs made	Cold end location	Miscellaneous
1	7-in. aluminum	Vermiculite	Hot and cold Nopak 4-way valves	Liquid air boiled by bubbling the main air thru it.	High pressure air only	1 through 3	Top	
2	3-in. aluminum	"	"	"	"	4 through 23* and 50 through 57	Bottom	
3	7-in. aluminum	"	Hot 4-way valve and cold check valves	"	Glass wool after both regenerators	58 through 76	Bottom	
4	7-in. fine steel	"	"	Expander	"	77 through 87	Bottom	
5	7-in. coarse steel	"	"	"	" and conical screens between regenerators and filters	88 through 100	Bottom	Piping enlarged. Additional "Knock-out drum" for removing entrained water from feed.
6	4½-in. copper	Mineral wool	Hot Homestead 4-way valve and cold check valves	"	Screens and cold filters removed. Two new filters installed.	101 through 127	Top	Equalizer to damp out temperature fluctuations provided. Regenerators were altered in length considerably in these runs.

* There were no runs numbered 24 through 49.

Once test conditions had been established and a steady state reached throughout the unit, pertinent temperature and pressure data were taken. Because of the unsteady nature of the process, temperature histories were obtained during the course of a cycle. Temperatures for both gas and regenerator packing were taken, although in many cases the extent of the packing temperature data was very limited. For each type of packing a series of runs was made in which the inlet temperature, flow rate, or cycle time was varied independently. In the case of the 4½ in. diameter copper packing, the regenerator length was also varied. Another variable studied to a rather limited degree was the effect of the ratio of high-pressure to low-pressure flow. Control of this variable was achieved by drawing off a fraction of the air

It was found that when treating air, containing water and carbon dioxide as impurities, complete removal of the carbon dioxide during the low-pressure phase of the cycle was not accomplished, and as a result, there was a gradual plugging of the regenerators, leading eventually to excessive pressure drops and a forced shutdown. As a result it was necessary to remove the CO_2 by scrubbing when making tests on the regenerators so that the necessary data on heat transfer were obtained without introducing the additional variables caused by plugging. Another impurity, which appeared to overtax the purification capacities of the regenerators, was entrained oil, and its thorough removal by filtration was found necessary. In the case of water the regenerators seemed to perform satisfactorily and no plugging trouble was

encountered from this source. The plugging with CO_2 can be explained on a theoretical basis as due to cold end temperature differences which were greater than the maximum permissible for re-evaporation during the low-pressure phase of the cycle. It was thought that in large plants this temperature approach could be reduced to the point where the regenerators could handle CO_2 satisfactorily. This was not found to be true and it was eventually discovered that carbon dioxide removal could only be accomplished in a reversing cycle by special procedures.

The experimental data on the regenerators presented a mass of information which proved rather difficult to reduce to a useful state for design purposes. This difficulty arose for the most part from the unsteady nature of the heat transfer process. Theoretical approaches investigated proved rather cumbersome for practical application. To provide some sort of correlation for design purposes, a rather simple and admittedly unsatisfactory method was used. From the observed data it was possible to compute the amount of heat transferred in a given regenerator per unit time. It was also possible to determine the average air temperature during each phase of the cycle at both ends of the regenerator. Considering the regenerator analagous to a recuperator, the average gas temperatures during each phase of the cycle define a temperature difference at each end of the regenerator. Using these temperature differences to fix the driving force, and knowing the heat load and packing area or volume of the regenerators, it was possible to calculate an overall heat transfer coefficient. Such a calculation involves certain assumptions which are not completely fulfilled in the regenerator, that is, that heat leak is negligible, and that there is no hysteresis in the metal packing. The nature of the assumptions introduces a note of uncertainty but it was felt that coefficients calculated in this manner would provide some comparison between the various packings tested and would be of some value for design purposes.

It was found that the heat transfer results could be correlated rather roughly by the following equation

$$U_H = A + B\left(\frac{M^{0.7}}{t_1^{0.3}\theta^{0.25}}\right). \tag{20}$$

in which U_H = overall heat transfer coefficient Btu per hr per ft² F.
M = average flow rate, moles per hr.
t_1 = entrance temperature, F.
θ = full cycle time, min.

The constants A and B have the following values:

Packing	A	B
3-in. aluminum	−1.71	+7.29
7-in. aluminum	−0.19	+1.90
7-in. coarse steel	−0.6	+3.47
7-in. fine steel	−0.28	+1.76
4½-in. copper	−0.38	+3.84

With equation (20) it is possible to compare the packings. Thus at a low value of the correlating group, for example, 0.3, these coefficients result:

Packing	U_H
4½-in. copper	0.77
3-in. aluminum	0.49
7-in. coarse steel	0.44
7-in. aluminum	0.38
7-in. fine steel	0.28

At a high value for the correlating group, for example, 0.8, these coefficients result:

Packing	U_H
4½-in. copper	2.69
7-in. coarse steel	2.18
7-in. aluminum	1.34
7-in. fine steel	1.13

It is therefore apparent that on an area basis, at least, the heat transfer coefficient is best for the 4½-in. copper packing.

If comparison on a unit volume basis is desired, the above coefficients should be multiplied by the following factors:

Packing	Conversion factor
3-in. aluminum	579
7-in. aluminum	535
7-in. fine steel	864
7-in. coarse steel	517
4½-in. copper	654

It is at once apparent that the copper packing maintains its superiority when compared on a volume basis.

For comparison on a weight basis, the following factors should be applied to the coefficients:

Packing	Conversion factor
3-in. aluminum	9.8
7-in. aluminum	10.56
7-in. fine steel	3.96
7-in. coarse steel	3.4
4½-in. copper	3.3

On this basis copper maintains its superiority to steel but it falls behind aluminum. However, a volumetric basis is generally of greater significance and it can be concluded with some assurance that the copper packing is best for heat transfer.

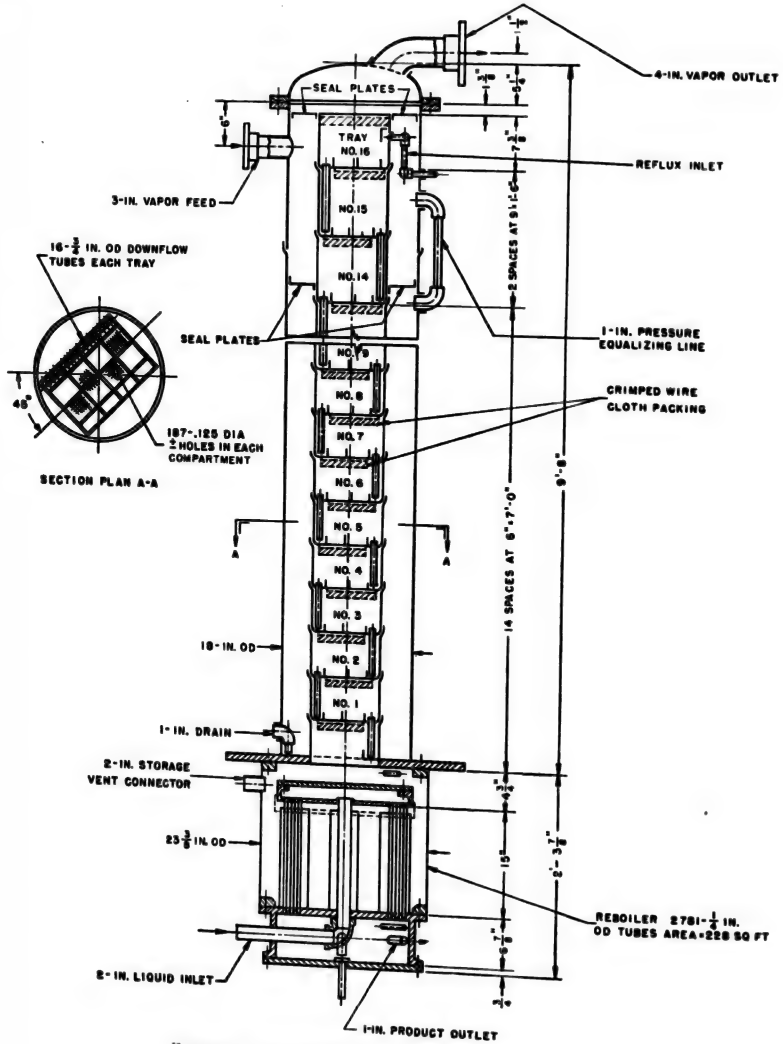


FIGURE 12. "J" tray fractionating tower showing regenerator.

In the course of each test run on the regenerators, pressure-drop data were taken but since in all cases the values were very low, no serious attempt was made to correlate the pressure drop information. During the low-pressure phase of the cycle when pressure drop becomes noticeable, values ranging from 1 to 6 psia were observed. The lowest pressure drop was exhibited by the 7-in. aluminum packing, after which followed in order of increasing pressure drop, the 4½-in. copper, 3-in. aluminum, 7-in. coarse steel, and 7-in. fine steel packing. For the original pressure drop data the reports cited earlier should be consulted.

In conclusion, it is felt that valuable information relative to the performance characteristics of regenerators was provided by the investigation.[6,15] Numerous difficulties were experienced but they were in the main overcome, and sufficient quantitative data were collected for design purposes. These data are complete enough to show the general performance to be expected and the effects thereon of the principal design conditions and operating variables. Later these data were used in the design of regenerators to be incorporated into oxygen plants. The regenerators performed satisfactorily except for plugging with carbon dioxide, a problem which became evident during the experimental studies.

7.12 REBOILERS

A typical condenser-reboiler used at the bottom of the single fractionating tower[6] is shown in Figure 12. The unit consists of a large number of small-diameter vertical tubes soldered to a fixed tube sheet at the lower end and to a floating head at the upper end. The cold air to be condensed enters the floating head and condenses on the inside of the tubes through transfer of heat to oxygen boiling on the outside of the tubes. The liquid air drains down into a collecting pot below the fixed tube sheet, and if the heat transfer surface is greater than necessary to accomplish the condensation, the liquid air level rises into the tubes to blank off the excess surface. Thus the condenser is self-controlling.[13,18] The oxygen vapor boiled off must flow radially outward to the outside of the floating head before rising into the fractionating section of the tower, but no serious vapor-binding in the closely spaced small tubes has been noticed.[6]

Since only a completely liquid stream leaves the condenser, the small quantities of noncondensable gases in the air, notably hydrogen and helium, unless appreciably soluble in the liquid air, will accumulate in the condenser and reduce the rates of condensation. It is standard practice to bleed off continuously a very small stream of gas from the condenser vapor space to prevent such an accumulation of noncondensables.

Reboilers are usually designed from a heat transfer standpoint using condensing coefficients predicted from conventional correlations and using boiling coefficients which have been obtained experimentally with a single copper cylinder electrically heated and immersed in boiling liquid. Boiling coefficients for air, oxygen, methane, and ethane were measured and the results[12] are shown in Figures 13 and 14. The lowest values are used for design purposes rather than the best correlation. Temperature differences

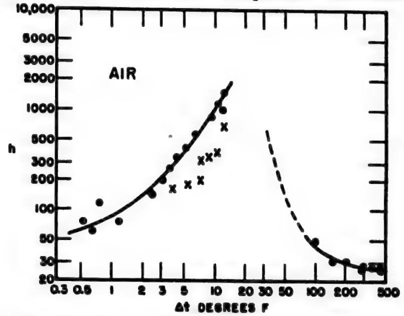


FIGURE 13. Individual heat transfer coefficient from metal to boiling air in Btu/(hr) (sq ft) (F).

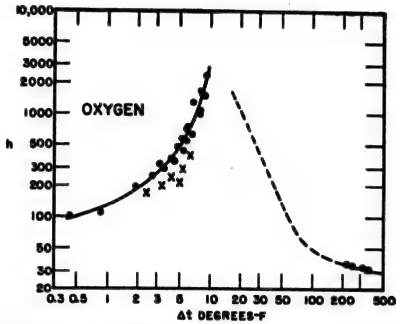


FIGURE 14. Individual heat transfer coefficient from metal to boiling oxygen in Btu/(hr) (sq ft) (F).

of about 10 F and overall coefficients of about 150 Btu hr^{-1} ft^{-2} F^{-1} are common. No reliable measurements of overall coefficients have been made, but plant operating experience indicates that coefficients predicted are conservative. A different type of reboiler using approximately countercurrent flow of boiling oxygen and condensing air, and effecting differential distillation of the oxygen, has been used and described.[10] An analysis of the theoretical advantage of this reboiler in improving fractionation has also been given.[4]

Chapter 8

LIQUID AIR FRACTIONATION

By *J. H. Rushton*

8.1 INTRODUCTION

IN THE WORK of Section 11.1 for the development of a number of oxygen-producing plants varying in size and in application, it soon became apparent that for most applications, units producing oxygen by the low-temperature fractionation of liquid air would be the most desirable, although considerable study and development would be needed to obtain the optimum in compactness, weight, simplicity and performance. Consequently, an extensive development program was initiated to provide the liquid air fractionation data so necessary to achieve the aims outlined.

This chapter covers the actual experimental data obtained in the program, performance data on operating units, and fundamental physical data pertinent to the study. The information is of use in the design of new units and in the analysis of results from and the evaluation of operating units.[1]

The following subjects are summarized:

1. Various types of liquid air fractionation systems.
2. The basis for correlation of tower performance.
3. Vapor-liquid equilibrium relationships and their use in tower design.
4. The efficiency and capacity of 23 different tower packings tested in a 2-in. laboratory column.
5. Performance tests on three types of packing and one type of tray in full-scale mobile oxygen unit towers.
6. Performance tests on nine different trays, six of which were developed by the use of an air-water testing technique.
7. Performance tests of Stedman packing and one type of tray on a rocking platform simulating the motion of ships at sea.
8. The performance and design of fractionating towers in the various units sponsored by NDRC.
9. Summary of data pertinent to the design of towers.

A list of the units which are discussed with respect to the fractionation equipment follows. All except the Independent Engineering Company plant are the result of NDRC development.

Designation of Unit	Description of Unit
M-1	M. W. Kellogg Co. high-pressure, two-trailer 1,000 scfh gaseous unit
M-2R	M. W. Kellogg Co. low-pressure, two-trailer 1,000 scfh gaseous unit
M-3	M. W. Kellogg Co. air-transported 400 scfh gaseous unit
M-4	W. F. Giauque high-pressure, single-trailer liquid (60–84 lb per hr) unit
M-5	M. W. Kellogg Co. low-pressure shipboard pilot plant liquid (400 lb per hr) unit
M-6	M. W. Kellogg Co.-Air Reduction Co. medium-pressure shipboard pilot plant liquid (400 lb per hr) unit
M-7	M. W. Kellogg Co.-Clark Bros. Co. Inc. low-pressure single-trailer 1,200 scfh gaseous unit
M-8	M. W. Kellogg Co.-Clark Bros. Co. Inc. low-pressure experimental gaseous unit
M-10	Air Reduction Co. high-pressure, single-trailer 400 scfh gaseous unit
M-11	F. G. Keyes high-pressure portable liquid (17–35 lb per hr) unit
M-12	Arthur D. Little-Latham high-pressure portable liquid (17 lb per hr) unit
M-13	Collins-McMahon low-pressure portable (150 scfh) gaseous unit
M-27	M. W. Kellogg-Central Engineering Laboratory low-pressure experimental gaseous unit
M-31	M. W. Kellogg-Central Engineering Laboratory Le Rouget experimental liquid unit
.....	M. W. Kellogg-Fort Belvoir experimental 800 scfh gaseous unit
.....	E. B. Badger Co. high-pressure portable liquid unit
.....	Independent Engineering Co. high-pressure mobile gaseous unit

As a result of the research program, NDRC now has available:

1. A close-spacing tray which is more efficient in the utilization of height in the larger installations than any other known fractionation medium.
2. Detailed information on the behavior in the fractionation of liquid air of twenty-three representative types of packing.
3. Vapor-liquid equilibrium data necessary for the prediction of tower performance.
4. Extensive and accurate knowledge of the operation of some different types of tower system. This, with the information on trays, packing and equilibria, enables a tower design to be made for any application.
5. Experimental information on the performance of some columns under rocking conditions.

8.2 FRACTIONATION OF AIR

The oxygen production of a unit is dependent upon the performance of each of its component parts. However, for any specified rate of oxygen production and purity, the efficiency of oxygen recovery from air in the distillation process plays a large part in setting the amount of air which must be handled by the unit, and hence the size of the equipment needed to supply and treat this air.

In the distillation or fractionation process, the liquid feed is introduced at the top of the tower and travels downward in intimate contact with rising vapor. The oxygen, less volatile than the other constituents of air, tends to concentrate in the liquid as it falls toward the bottom of the tower. Here the liquid is reboiled, and the product may be withdrawn as either liquid or vapor. The vapor formed by reboiling rises up the tower countercurrently to the liquid. The amount and purity of the product which may be withdrawn depend upon the length of the region in which the vapor-liquid contacting occurs, and the efficiency with which it is accomplished. This means that for any given percentage of oxygen recovery and efficiency of contacting, one dimension of a tower, the height, is independent of the size of the oxygen unit. Therefore, in order to keep the tower size commensurate with the unit size in small plants it was necessary either to find some means of increasing the contacting efficiency, or to accept a lower oxygen recovery.

In distillation, two general types of towers are in use: one in which the vapor-liquid contacting is done successively in bubbling plates or trays, and the other in which the tower is filled with some sort of packing, to increase the wetted area available for continuous vapor-liquid contacting.

At the beginning of the project no data were available on the use of packing in liquid air fractionation and only a very meager amount on the use of tray towers. The available information indicated that towers used in the oxygen industry varied from 10 to 20 ft in height. Since the available tower height was limited, it was necessary to study fractionation equipment, its operation, and some of the fundamental physical data of air.[2]

8.2.1 Tower Systems

There are a number of different arrangements of fractionating towers in use in the separation of oxygen from liquid air. Some of the more common systems are shown in Figure 1. The choice of system to be used in any particular unit depends upon a number of factors which include, among others, the type of liquefaction or refrigeration cycle used.

Simple Single Liquid Feed Tower

This is the simplest of all the liquid air fractionation columns, and can be used with any refrigeration cycle. The high-pressure air feed is condensed in the reboiler by the vaporizing oxygen. The condensed air is expanded through a valve down to the tower pressure and introduced at the top of the fractionator. The liquid travels downward through the tower in countercurrent contact with the rising vapors. Oxygen may be withdrawn either as vapor or liquid product from the boiling side of the reboiler, while the waste gas passes out the top of the tower.

A fraction of the high-pressure liquid is vaporized in expanding to the tower pressure. This lowers the quantity of liquid reflux fed to the tower and decreases the oxygen recovery. This effect may be partially overcome by subcooling the liquid by heat exchange with the waste nitrogen. The condensing pressure should thus be kept as low as possible but the proper heat transfer in the reboiler should be maintained.

Because the liquid feed at the top of the column is air, the waste overhead gas always contains an appreciable amount of oxygen. At atmospheric pressure this fact limits the oxygen recovery to about 60 to 70% of the oxygen in the air feed. Increasing the tower pressure decreases the maximum recovery by lowering the relative volatility of oxygen and nitrogen.

The maximum theoretical recovery as a function of tower pressure is shown in Figure 2. Two cases are shown, one in which the operating conditions are those encountered in actual towers, and the other, the idealized case in which the liquid condenses at its minimum pressure (that is, with zero temperature difference across the reboiler), is subcooled, and with no heat leak to the column.

The height restriction in the portable units indicated the use of single towers, even though the low oxygen recovery is a disadvantage. Some of the towers, such as the one in the Collins-McMahon unit,[3] are too short even to approach the theoretical recovery. Often when the oxygen is withdrawn as liquid product, the yield is limited by the amount of refrigeration available, rather than by the distillation process. In this case the lower maximum yield of a single tower is not a disadvantage.

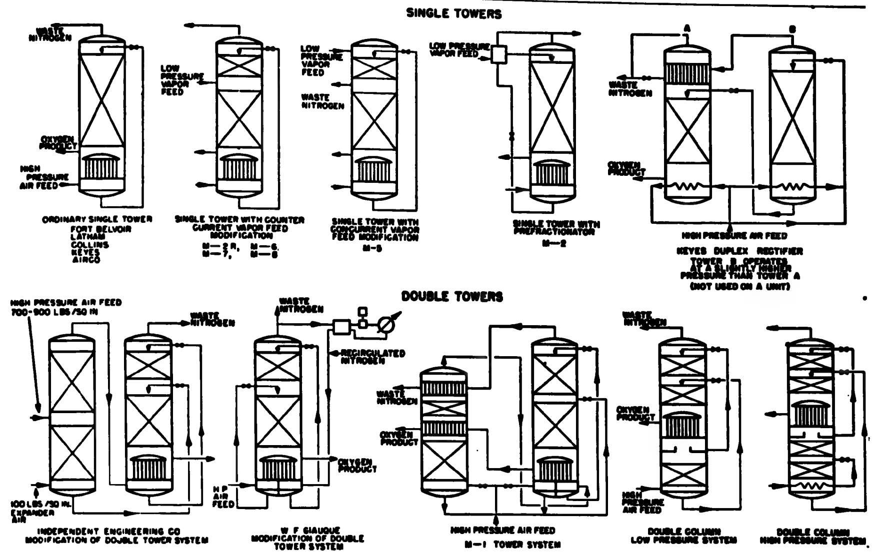


Figure 1. Liquid air fractionation tower systems.

Another advantage of the single tower is its simplicity of operation. Since expert personnel may not always be available for operation of these units, this item is of importance.

Single towers have been used in most of the units built for the Armed Forces.

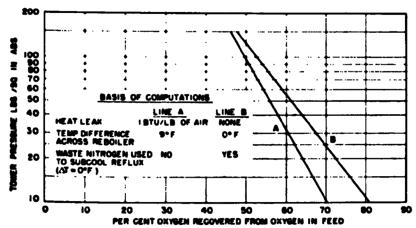


Figure 2. Effect of pressure on maximum theoretical oxygen recovery for single tower operation.

Single Tower with Vapor Feed Modifications

In some low-pressure units, refrigeration is supplied by expansion of a part of the air supply through an engine to tower pressure. Air so used does not go to the condenser and is thus lost to the recovery system as liquid feed, but some of the oxygen may be recovered from this vapor if it is contacted with the liquid feed. This may be done either countercurrently as in the M-7 unit, or concurrently, either inside the tower as in the M-5 unit, or outside of the tower with a prefractionator as in the M-2 unit. The choice between these two alternatives depends upon the height available, the mechanical design of the tower system, and the specific purpose of the unit. The effect of these factors on the M-5 design is discussed later.

Concurrent contacting is equivalent to an equilibrium flash vaporization of air in which the liquid composition may vary from 21% oxygen at 0% vapor to 50% oxygen at 100% vapor. This contacting of liquid and vapor feeds does not change the quantity of liquid reflux but instead provides a richer feed to the fractionating section, and by so doing gives a higher oxygen recovery.

With an infinitely large ratio of vapor to liquid feed, there is no difference between the two methods of contacting. However, with the ratio of liquid to vapor encountered in this program, a higher oxygen

recovery is made by using the countercurrent system. The introduction of vapor feed at some intermediate point in the tower forms a rectifying section in which some of the oxygen in the vapor feed may be stripped out.

With either of these systems the maximum theoretical recovery of oxygen is about 125% of the oxygen in the liquid feed.

For the conditions encountered in the portable units the vapor feed system probably gives a better utilization of height than the double tower system. The units built by Clark Brothers Company have columns of this type.

Keyes Duplex Rectifier

Although this system has two towers it is still a single column in principle. It has not yet been used on a unit, and is included here as an example of one of the many possible arrangements which can be used to reduce column height. The two columns fractionate the liquid in series. The crude oxygen from the first is purified in the second. At the top of the second tower the waste nitrogen condenses some crude oxygen vapor, thereby furnishing more reflux. It is a modification of the subcooler principle and can give an absolute maximum yield of not over 75%.

Simple Double Column

It has been mentioned that the yield of a single column is limited because of the oxygen content of the liquid air feed. The term double column refers to a fractionating tower which has, below the reboiler, a rectifying section in which pure nitrogen reflux is produced. Two types of standard double towers are shown in Figure 1. Neither of these has been used on an NDRC unit.

In the simpler of these two types the high-pressure air feed is introduced at the bottom of the lower section. Reflux to this fractionating section is furnished by condensing nitrogen in the reboiler by means of the boiling oxygen. About 40% of the air feed is withdrawn as liquid nitrogen from the top of the high-pressure section and introduced as reflux at the top of the low-pressure section. The remaining fraction of the liquid air feed is taken from the bottom of the high-pressure section and introduced somewhere near the center of the low-pressure section.

In the system described, the maximum yield calculated from present equilibrium data is about 90% of the oxygen in the liquid air feed. With vapor feed in the low-pressure tower, the recovery can approach 125% of the liquid feed as it does with the single tower with vapor feed.

Compound Double Column

The second type of double column may be used when the head pressure is high enough to use another reboiler in the bottom of the high-pressure tower. The liquid from this condenser may be then introduced at a mid-point in the high-pressure tower. With this modification it is possible to recover practically 100% of the oxygen in the total air feed, assuming no vapor feed.

Aside from the obvious advantage of complete oxygen recovery, this column can simultaneously produce a pure inert gas from the top of the tower. This system is out of the question for portable units unless an ultraefficient tower packing is developed.

A disadvantage of both double types of double columns is the difficulty of control, as there are three streams to be analyzed, and three liquid levels to be controlled. However, the experimental column of the M-31 plant was found to be about as easy to control as the single columns.

Independent Engineering Company Double-Tower System

This system, as orginally used on the mobile oxygen units manufactured by the Independent Engineering Company of O'Fallon, Illinois, is an attempt to reduce the height of a double tower by placing the high and low-pressure sections side by side. However, when this is done, there is no way in which reflux may be supplied to the top of the high-pressure tower.

In the cycle used in these units,[6] a portion of the high-pressure air feed is expanded through an engine from about 800 psi to 100 psi. This air is fed as vapor to the bottom of the high-pressure tower. The remainder of the air compressed is introduced at the mid-point of the high-pressure tower. The quantity of liquid reflux at this point is set by the heat balance of the tower system and is about 10% to 15% of the total amount of air.

The liquid, which contains about 40% oxygen, withdrawn from the bottom of this tower is fed to an intermediate point in the low-pressure tower. The overhead high-pressure vapor is condensed in the reboiler and then fed as reflux to the top of the low-pressure tower. The theoretical maximum oxygen recovery with this system is about 10% greater than is possible with a single liquid feed tower.

M-1 Double-Tower System

This tower arrangement is an attempt to attain double tower yields in a limited height.

The low-pressure tower has a reboiler which is divided into two sections on the condensing side. Part of the high-pressure air feed is liquefied in one of these sections. The remainder of the air feed is sent to the bottom of the high-pressure tower, where it is fractionated. Reflux is supplied by the latent heat of vaporization of the vaporizing liquid oxygen product and the sensible heat of the waste gas from the low-pressure tower. Uncondensed vapor passing through this condensing section is then liquefied in the second section of the reboiler from which the liquid is fed to the top of the low-pressure tower. The liquid from the bottom of the high-pressure tower is mixed with the condensed air and introduced to an intermediate point in the low-pressure tower. The maximum theoretical oxygen yield of this system should be 95% to 100%.

Giauque Modification of the Double Tower

This tower is classed under double towers because nitrogen reflux is prepared outside of the low-pressure column. In this alteration of the double-tower system a 100% oxygen yield may be made by recirculating the tower overhead to increase the amount of liquid reflux.

In the system, as planned by Giauque of the University of California for his portable unit for NDRC, the tower is built with the condensing side of the reboiler divided into two sections.[7] The high-pressure air feed is liquefied in one of these sections and then fed to some intermediate tray in the tower. Part of the waste gas leaving the tower is warmed to room temperature, compressed to about 100 psi, recooled and then liquefied in the second section of the reboiler. From here the liquid is fed to the top of the tower.

By increasing the amount of recirculated nitrogen, the separation of oxygen from liquid air is made easier, and the tower may be shortened. It is possible to make a perfect recovery of the oxygen in the incoming air in a very short tower, but this benefit will be at the expense of power and of refrigeration loss in the recirculating nitrogen. In order to attain the perfect oxygen recovery, the theoretical minimum amount of nitrogen which must be recompressed is 70% of the air feed.

8.3 THEORY OF LIQUID AIR FRACTIONATION

8.3.1 Basis of Correlation

The research in liquid air fractionation has followed two definite lines, namely, fractionation in laboratory size equipment and in towers of the size used in portable units. Some basic measure of fractionating ability must be used to reconcile the effects of height, diameter, liquid and vapor loads, type of packing or trays, distributors, redistributors, etc., in the correlation of data, as well as in the design of a new tower.

In studying distillation in packed towers either one of two concepts is generally used as a yardstick: (1) the transfer unit, and (2) the theoretical plate. These are used as the height of packing in a transfer unit [HTU] and the height of packing equivalent to a theoretical plate [HETP].[1]

It is often said that the HTU is the better unit to use because it is based upon valid integration of a fundamental relationship, while the use of the HETP applies a continuous batch contacting mechanism to a continuous countercurrent process. Actually, both units are functions of the absorption rate coefficients. The units are also dependent upon the value of the ratio of slope of the equilibrium line to the slope of the distillation operating line. This means that for any one system the HTU and HETP will vary with the reflux ratio. This variation with reflux ratio is apt to be greater for the HTU than for the HETP.

These same two concepts are used in evaluating the performance of tray towers, in which application they appear as plates per transfer unit [PTU] and as overall tray efficiency. However, the use of PTU in tray towers is also subject to the criticism that a mechanism is implied which does not exist.

In the research program towers made of both trays and packings have been investigated. Comparison of these two types cannot be simple unless one of the above concepts is used for both cases. Although there is not much choice between the HTU and the HETP, since whichever is used is theoretically unsound in half its application, the HETP has been chosen as a basis throughout this study because tray efficiencies are in much more common usage than the PTU.

In addition, it is much easier to visualize the concept of tray efficiency and of HETP than of transfer units.

8.3.2 Methods of Tray Calculation

The composition of air is generally accepted as:

Component	Mole per cent
Nitrogen	78.03
Oxygen	20.99
Argon	0.933
Carbon dioxide	300×10^{-4}
Hydrogen	100×10^{-4}
Neon	15×10^{-4}
Helium	5×10^{-4}
Krypton	1.1×10^{-4}
Xenon	0.08×10^{-4}

For all practical purposes the traces of rare gases may be considered negligible, so that air is treated as a three-component mixture of the following composition:

	Mole per cent	Atmospheric Pressure Boiling Point
Nitrogen	78.08	−320.4 F
Oxygen	20.99	−297.4 F
Argon	0.93	−302.3 F

Fractionation of air is sometimes considered as the separation of a binary mixture of nitrogen and oxygen. This simplified treatment often leads to erroneous conclusions. For instance, calculations with the oxygen-nitrogen binary mixture show that five perfect plates are required at total reflux to make 99.5% oxygen, but that only 6.5 are needed to make 60% recovery at the same 99.5% purity. This is in startling contrast to operating experience. Because the boiling points of oxygen and argon are so close together, the upper part of the single tower acts as a nitrogen stripper, with the argon concentration reaching a maximum somewhere in the tower. This maximum concentration may be as much as 25 to 30% depending upon the reflux ratio. Below the point of maximum argon concentration the presence of nitrogen is negligible and the tower then acts essentially as an argon stripper. This sort of behavior is typical of most multi-component distillations.

Methods of tray-to-tray calculations have appeared frequently in the literature. All the methods are fundamentally the application of successive heat and material balances to the concept of the perfect tray, which is defined as one in which the vapors leaving the plate are in equilibrium with the liquid leaving the plate.

Computation of single feed liquid air fractionation is considerably simplified by the fact that the tower is only a stripping section and that the amount of nitrogen present in the oxygen product is insignificant. Since only a stripping section is involved, the complicated calculations necessary to determine the proper location of the feed tray are eliminated. The absence of nitrogen in the product makes it possible to calculate from the top to the bottom directly. If nitrogen were present in the bottom product in an appreciable amount, it would be necessary to assume a bottoms composition and compute upwards to the feed tray. This process leads to a long series of trial and error calculations. Before any tray calculations were made, the validity of the assumption that the effect of nitrogen is negligible was checked by the method of Thiele and Geddes. For instance, if ten perfect trays are used, it was found that at 25% oxygen recovery, the mole fraction of nitrogen in the product is 0.00001.

If the number of trays in a tower is very low, then, of course, the amount of nitrogen in the product will be appreciable and must be considered. Actually this case has not occurred in the data taken. Short packed columns sometimes had the effect of very few theoretical trays, but since these towers were tested at total reflux, no product was withdrawn, and the amount of nitrogen in the bottom does not appear in the calculations.

The method used here is, therefore, simply one in which heat and material balances and the equilibrium calculation are repeated for each tray from the top to the bottom. Due to heat leak and the fact that the molal heat of vaporization differs from those of argon and oxygen, it is necessary to correct the liquid and vapor quantities on each tray by successive heat balances. When the nitrogen content has become low enough, for example, 0.04 to 0.05 mole per cent, the stepwise balances may be omitted and the simple graphical method used. Algebraic tray calculations frequently become tiresome, especially at the higher oxygen yields where the number of steps is large. Use of a graphical method, devised for treating the fractionation of ternary mixtures simplified the work. This method was used in checking calculations.[1]

A number of stepwise calculations have been made to determine the number of theoretical trays required for various oxygen recoveries and purities. These calculations are summarized by Figure 3 in which the oxygen concentration in the liquid leaving

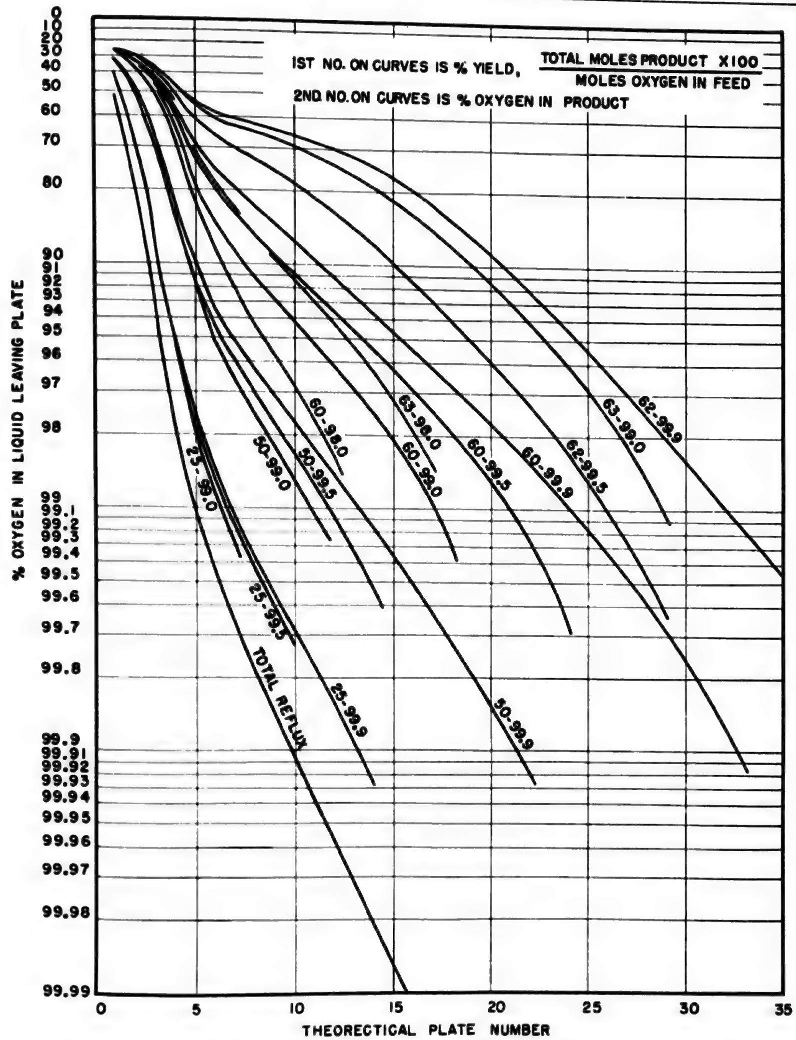


FIGURE 3. Relation between oxygen concentration in liquid or plates for various yields and production purities.

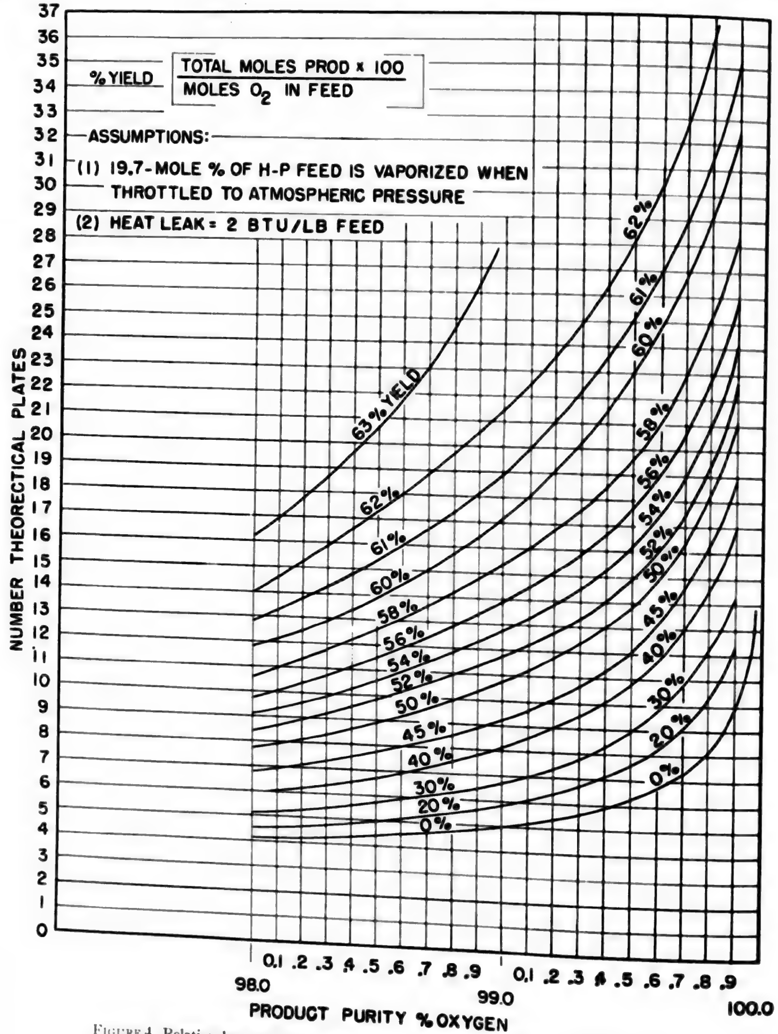


FIGURE 4. Relation between production purity and number of plants at constant yield.

each theoretical tray is given. By cross-plotting of these lines, it is possible to construct Figures 4 and 5, which give the number of theoretical plates required to produce a given purity at any operable yield.

Figure 4 is based upon average single-column operating conditions of:

Tower pressure	20 psia
Condensing pressure	90 psia
Heat leak	2 Btu per lb of air
No reflex subcooling	

The chart will not be greatly in error if used for any simple single tower at an oxygen recovery of 50% or less. It may be used for oxygen recoveries as high as 60% if the conditions are such that the

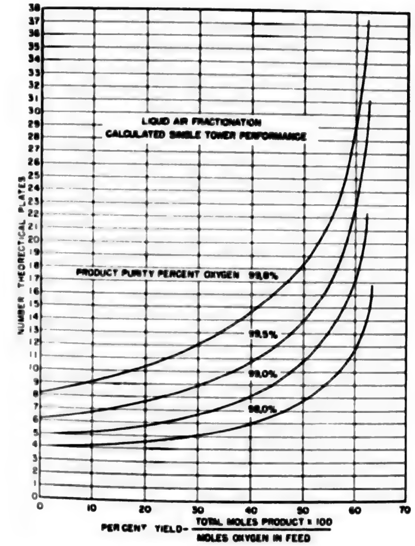


FIGURE 5. Relation between yield and number of plants.

amount of vaporization resulting from expansion of the reflux is within 20% of that of the specified conditions. Above a recovery of 60% the chart becomes doubtful because of uncertainties in the equilibrium data.

Figure 6 shows the error in estimating HETP's caused by inaccurate analysis of the oxygen product. Although the error in the actual number of trays becomes greater with increasing recovery, oddly enough the percentage error is practically independent of the oxygen yield at any given analytical error and purity.

The case of vapor feed towers has not been given such a thorough treatment because of the problem of locating the vapor feed. At any given ratio of vapor feed to liquid feed and oxygen recovery, there is one and only one correct location of the vapor feed. Therefore, any complete analysis of a vapor feed tower must consider five variables; product quantity and purity, vapor quantity, feed tray location, and total number of trays. Even if such an analysis were made it would serve only as corroboration of HETP's

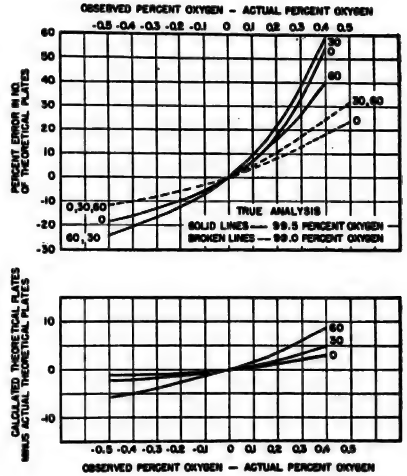


FIGURE 6. Effect of errors in oxygen analysis on tray calculations.

and tray efficiencies found in single-tower operation. The performance of several tower runs with vapor feed has been checked,[9,12] and where analyses at the feed tray were available the results agreed closely with those runs using liquid feed only. Comparison of HETP and HTU has been investigated[1] and it has been found that HETP and HTU are both equally applicable.

8.4 VAPOR-LIQUID EQUILIBRIUM

The importance of good equilibrium data cannot be overestimated if engineering methods are to be applied in the design of oxygen units. The effect of unreliable data may be minimized by testing towers at total reflux, but such experiments can be used only comparatively without knowledge of equilibrium behavior.

Equilibrium data may be presented in a number of ways. In this work either the equilibrium constant, $K = y/x$, or plot of y vs x, is used where y and x are the equilibrium mole fractions of a component in the vapor and liquid phases, respectively. The function K is more convenient in the three-component tray calculations, while y vs x is used in the binary graphical solutions.

There were no reliable vapor-liquid equilibrium data available on the three-component system N_2-A-O_2, and research was initiated to obtain them,[13] but the three-component data (Figure 7) were obtained too late to be used for the plants covered in Chapters 3 and 4.

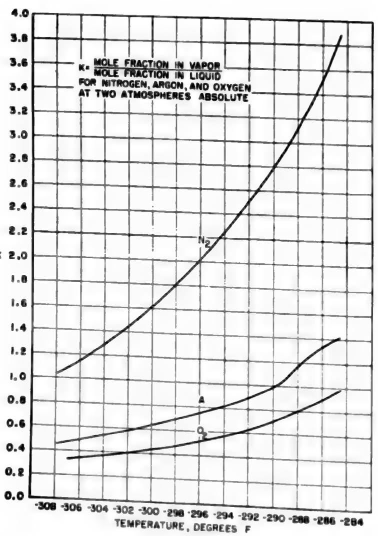


FIGURE 7. Equilibrium data for the system nitrogen-argon and oxygen at two atmospheres absolute.

Published and NDRC experimental data on the three possible binary systems are: oxygen-nitrogen (Figures 8 and 9), argon-nitrogen (Figure 10), argon-oxygen (Figure 11).

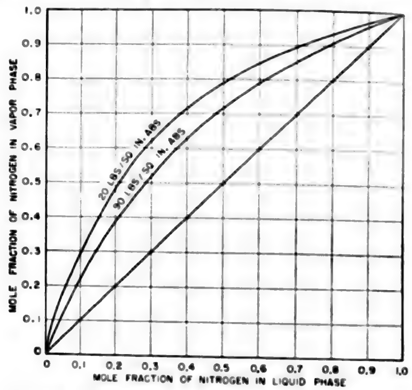


FIGURE 8. Liquid-vapor equilibriums for the oxygen-nitrogen system.

The ideal equilibrium constants computed by Raoult's and Dalton's laws are shown with the experimental values for the binary systems. The agreement between the ideal and actual values is very good except in the cases of low concentration of one component. Because of this agreement, it seemed reasonable to assume that the ternary system would also behave ideally. The deviations from the ideal equilibrium constants occur in composition ranges which are not encountered in liquid air fractionation, except in the removal of nitrogen, and in the section of a tower where only argon and oxygen are considered. Data used for column design are given in Table 1.

Fortunately nitrogen is so much more volatile than oxygen or argon that it is stripped out very quickly, so that a considerable error in the nitrogen K makes little difference in the oxygen and argon composition. When the nitrogen is out, the Aston data are applicable.[19]

8.5 TRAY EFFICIENCIES

In evaluating the efficiency of mass transfer in trays two different concepts are used. These are the Murphree efficiency and the overall tray efficiency. The Murphree efficiency is defined as the change in composition that would be accomplished

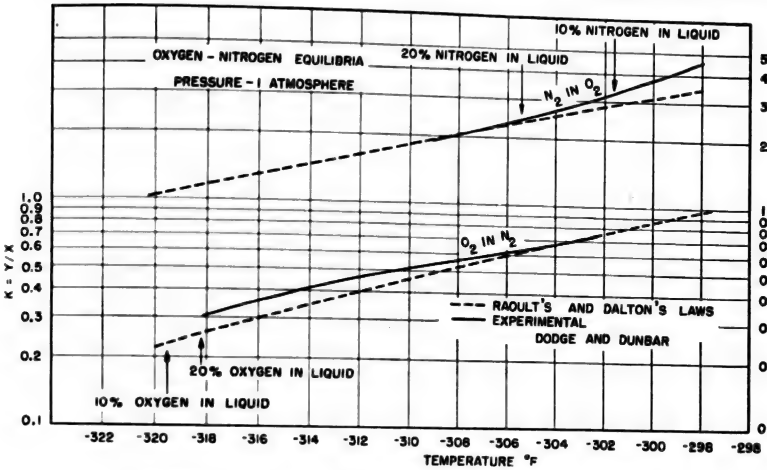


FIGURE 9. K values for oxygen-nitrogen equilibriums, 1 atmosphere absolute.

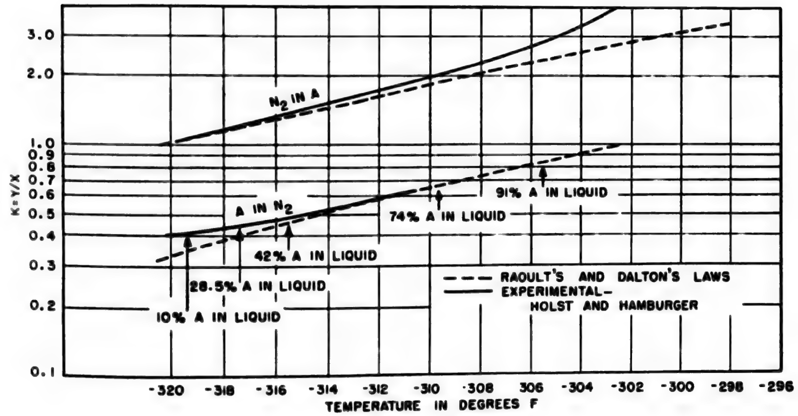


FIGURE 10. Equilibrium data for argon-nitrogen, 1 atmosphere absolute.

[illegible] vapor leaving were in equilibrium with the [illegible] overflow. This definition when applied to a [illegible] point of vapor-liquid contact is known as the [illegible] point efficiency. The overall efficiency is [illegible] ratio of the number of perfect trays necessary for a given separation to the number of actual trays required for the same task.

The Murphree and overall tray efficiencies are equal only when the equilibrium and operating lines are parallel. The relation between the point efficiency

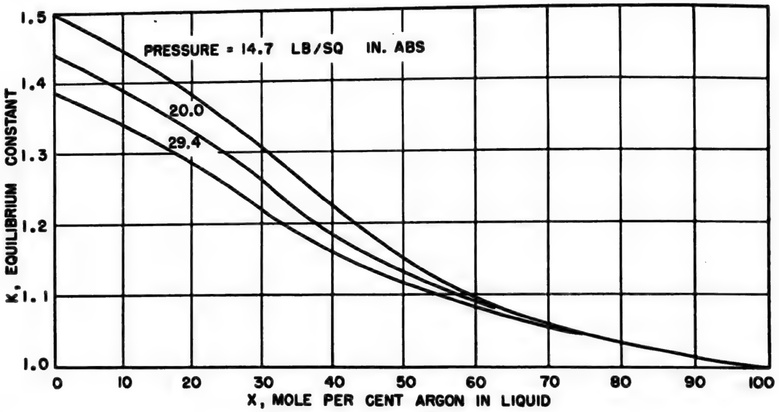


FIGURE --. Equilibrium constants for argon-oxygen.

TABLE 1. Nitrogen-argon-oxygen vapor-liquid equilibrium constants. $K = y/x$ vs temperature at 1 atmosphere abs.

Temp F	N_2	A	O_2	Temp F	N_2	A	O_2
−316.0	1.26	0.465	0.358	−301.5	3.30	1.06	0.775
−315.5	1.30	0.475	0.370	−301.0	3.45	1.15	0.810
−315.0	1.32	0.490	0.385	−300.5	3.60	1.22	0.830
−314.5	1.36	0.500	0.398	−300.0	3.77	1.29	0.850
−314.0	1.40	0.515	0.410	−299.9	3.80	1.30	0.860
−313.5	1.44	0.530	0.420	−299.8	3.84	1.32	0.865
−313.0	1.48	0.545	0.435	−299.7	3.88	1.33	0.870
−312.5	1.53	0.560	0.450	−299.6	3.91	1.34	0.875
−312.0	1.58	0.575	0.460	−299.5	3.95	1.35	0.880
−311.5	1.62	0.590	0.475	−299.4	3.99	1.36	0.888
−311.0	1.67	0.605	0.485	−299.3	4.02	1.37	0.895
−310.5	1.72	0.620	0.500	−299.2	4.06	1.38	0.900
−310.0	1.77	0.640	0.512	−299.1	4.10	1.39	0.905
−309.5	1.82	0.660	0.525	−299.0	4.15	1.40	0.910
−309.0	1.89	0.680	0.538	−298.9	4.20	1.41	0.917
−308.5	1.95	0.700	0.550	−298.8	4.23	1.42	0.923
−308.0	2.01	0.720	0.563	−298.7	4.27	1.43	0.930
−307.5	2.09	0.740	0.577	−298.6	4.30	1.44	0.937
−307.0	2.15	0.765	0.590	−298.5	4.35	1.45	0.943
−306.5	2.23	0.790	0.600	−298.4	4.40	1.46	0.948
−306.0	2.30	0.820	0.620	−298.3	4.45	1.47	0.955
−305.5	2.40	0.840	0.630	−298.2	4.48	1.48	0.961
−305.0	2.50	0.860	0.645	−298.1	4.52	1.49	0.968
−304.5	2.60	0.890	0.660	−298.0	4.55	1.50	0.975
−304.0	2.70	0.920	0.680	−297.9	4.60	1.50	0.980
−303.5	2.80	0.950	0.700	−297.8	4.65	1.50	0.985
−303.0	2.90	0.980	0.715	−297.7	4.70	1.50	0.992
−302.5	3.05	1.000	0.730	−297.6	4.75	1.50	0.997
−302.0	3.18	1.03	0.750	−297.5	4.80	1.50	1.000

and the tray efficiency is ... of the degree of **liquid and vapor mixing** ... flow effect in the **tray. Figure 12 shows** this ... for these types **of trays.**

In designing a tower, of course, only the overall efficiency is of any use and it is this overall efficiency of the trays studied which has been used in the correlation of tower performance.

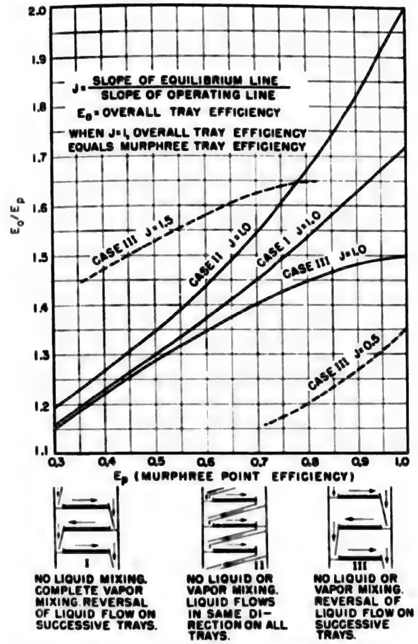


FIGURE 12. Effect of direction of flows on tray efficiencies.

8.6 EFFECT OF TOWER PRESSURE

Atmospheric pressure equilibrium constants have been used exclusively although tower pressures have varied from 15 psia to 22 psia in the bulk of the experimental work, and pressures as high as 45 psia have been reached. Argon-oxygen data at pressures greater than atmospheric were not available in time to permit use in the initial designs.

The effect of pressure on mass transfer is threefold. The maximum theoretical yield decreases with increased pressure; the number of trays required to reach any yield increases with pressure; and pressure tends to reduce the rate of mass diffusion. As far as present experience goes, use of the McCabe-Thiele analysis with Figure 8, and the treatment of argon and oxygen as a single component are satisfactory for predicting the maximum yield (infinite plates).

To determine the increased difficulty of fractionation evidenced by the additional plates required, the three-component data are necessary as well as the correct oxygen-argon relationship. Although pressure may have a large influence on the number of theoretical trays required, no serious error will occur in design of production towers if their operation is at substantially the same pressure as the test towers from which the efficiencies and HETP's were derived.

Unfortunately, there are no performance data which show clearly the loss in oxygen recovery caused by high-pressure operation.

8.7 EXPERIMENTAL PROGRAM

8.7.1 Small Column Tests

The equipment and flowsheet for the liquid air fractionation (small column) tests are shown in Figures 13 and 14.[1,14,15]

Table 2 gives a list of the packings tested and a

TABLE 2. Yale University test data summary of packing efficiencies and capacities in two-inch diameter tower.

Packing	Packed density lb per cu ft	Flooding capacity lb per (hr) (sq ft)	HETP at flooding point
Berl saddles, ¼ x ¼ in. ..	60	1,520	2.7*
Carding teeth		2,520	7.4
Ewell spiral packing (1-in. dia.)	...	350	...
Fiberglas No. 1	0.72	1,970	8.6
Fiberglas No. 1	1.79	1,510	6.9*
Fiberglas No. 1	4.3	...	6.9*
Fiberglas No. 2	21.4	...	8.6*
Fiberglas No. 3	10.7	1,490	6.9*
Haydite, 4–8 mesh	25	1,100†	2.7*
Haydite, ⅜ in.	25	1,450	4.4*
Helices, ⅛ in. single turn, glass	43	1,500‡	4.2*
Helices, $^3/_{32}$ in. single turn, wire	83	1,450	6.4
Regenerator packing	54	1,070	4.7*
Rings, ¼ in. aluminum Lessing		1,550	2.0
Rings, ¼ in. glass, 10 in. packed height		1,120	1.6
Rings, ¼ in. glass, 18 in. packed height		1,380	1.9
Rings, ½ in. glass		2,300	4.2
Rings, $^3/_{32}$ in. long shoe eyelets	55	1,630	2.0
Stedman, 60 x 40 mesh ...	33	1,700	1.2
Stedman, 80 x 80 mesh ...	18	1,400	1.28
Stedman, 100 x 100 mesh..		1,500	1.35
Stedman, 120 x 120 mesh..		800	2.0
Textile, metal-wire 0.006 in. dia.	17	2,660	5.9

* Tower inclination not measured; known to be vertical in all runs not so marked.
† Flooding capacity is liquid or gas rate (total reflux) at the top of the tower, measured at 1 atm pressure.
‡ Capacity estimated from the pressure drop, value of HETP given is at 1,000 lb per (hr) (sq ft) feed rate.

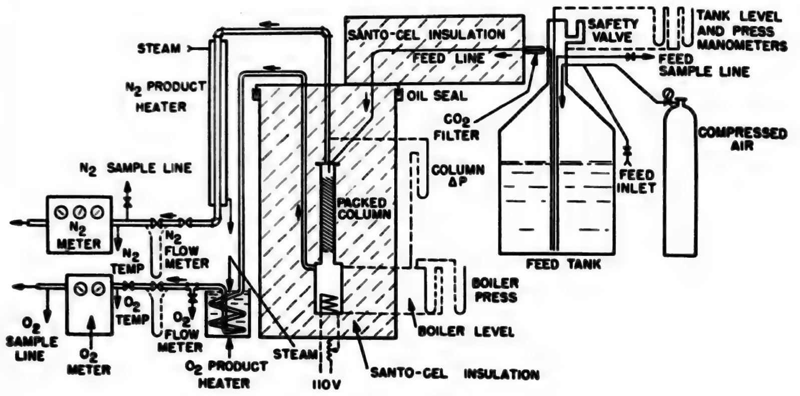


FIGURE 13. Small test column setup.

summary of the packed densities, capacities, and the HETP's at the flooding point. The efficiency of the packing is, in most cases, the highest at the flooding point.

The HETP and pressure drop data are summarized in the following graphs: HETP vs feed rate, tower known to be vertical (Figure 15), HETP vs feed rate, inclination of tower not known (Figure 16),

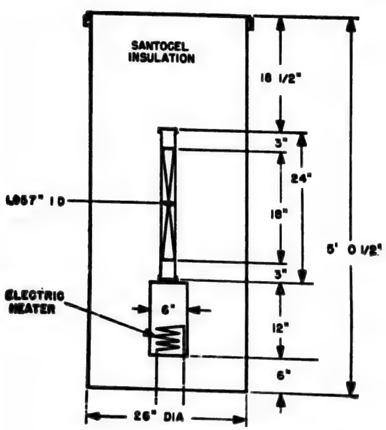


FIGURE 14. Dimensions of small test column.

pressure drop vs vapor rate, Stedman packing (Figure 17), pressure drop vs vapor rate, other packing (Figures 18 and 19), efficiencies and capacities (Figure 20).

EFFECT OF TOWER ALIGNMENT

During the tests with Stedman packing the importance of the tower inclination was discovered. A column was insulated merely by lowering it carefully into the cold box, which was filled with Santocel. With this technique it was possible for the tower to lean slightly. Several packings had been tested before the importance of this factor had been discovered. The more interesting of these were retested in a tower known to be vertical.

After this discovery, the effect of inclination upon efficiency was determined quantitatively for Stedman packing, shoe eyelets and glass rings. These results are plotted in Figure 21. Stedman packing appears to be more sensitive to inclination than either of the bulk packings. At an angle of 2 degrees from the vertical the efficiency of the Stedman packing is 40% lower than when vertical. The same tilt decreases the efficiency of shoe eyelets and ¼-in. glass rings by 25% and 15% respectively. In addition, inclination increases the capacity of Stedman packing. The flooding point in the early runs is as much as 50% higher than the capacity determined in the vertical tower. Although no flooding points were obtained for the bulk packing, when tilted, the pressure drop was not

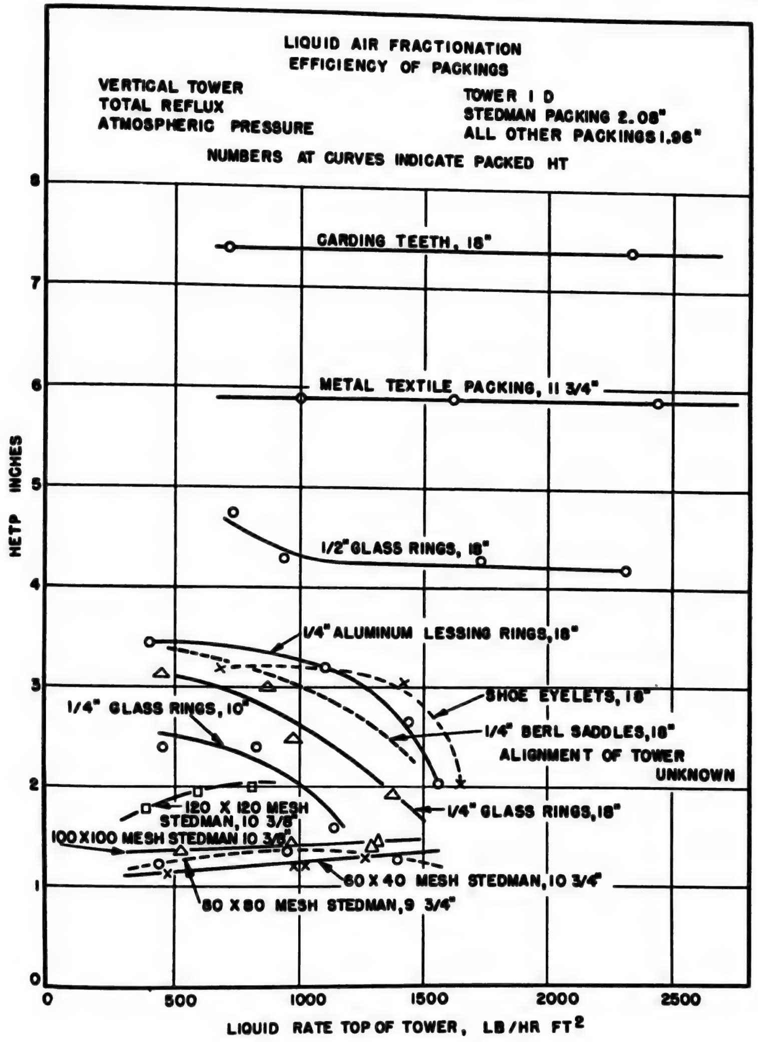


FIGURE 15. Packing efficiencies.

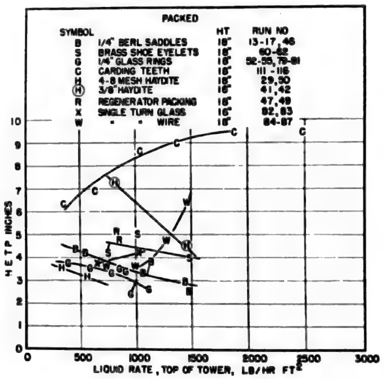


FIGURE 16. Packing efficiencies.

greatly affected. This might indicate that the capacity is not altered by the inclination.

Description of Packings Tested

The following is a description of the packings in the order in which they appear in Table 1, a few of which are shown in Figure 22.

Berl Saddles. This is a saddle-shaped packing, manufactured by Maurice A. Knight, Akron, Ohio. Only ¼-in. size semi-porcelain saddles were tested. This packing was tested first because it has the reputation of being one of the most efficient of all tower packings. All tests with it were made before the importance of the verticality was discovered. The fact that the Collins-McMahon 4-in. diameter column packed with saddles performs better than the 2-in. Yale column suggests that the latter tower was not vertical when tested.

Carding Teeth, Wire and Glass Helices. These packings were first studied in small laboratory columns. They were found to be rather efficient, having HETP's as low as 2 in. with the system heptane-methyl cyclohexane. It is reported also that the HETP's vary over a threefold range, depending upon the wetted condition of the packing.

Carding teeth are similar to rectangular hairpins. The particular batch tested contained teeth about ⅛ in. wide and ¼ in. to ½ in. long. The single-turn helices are exactly what the name implies, a wire helix of one turn.

The carding teeth were tested in a vertical column; the tests with helices may or may not have been in a vertical tower. When tested in a tower not known to be vertical, all three of these types showed HETP's which increased with throughput. Outside of a similar slight tendency in the 120-mesh Stedman packing, these are the only instances encountered in

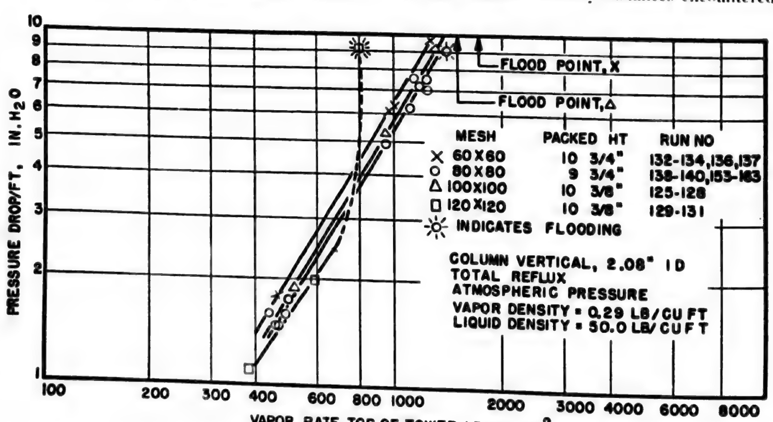


FIGURE 17. Relation between pressure drop and vapor rate for Stedman packing.

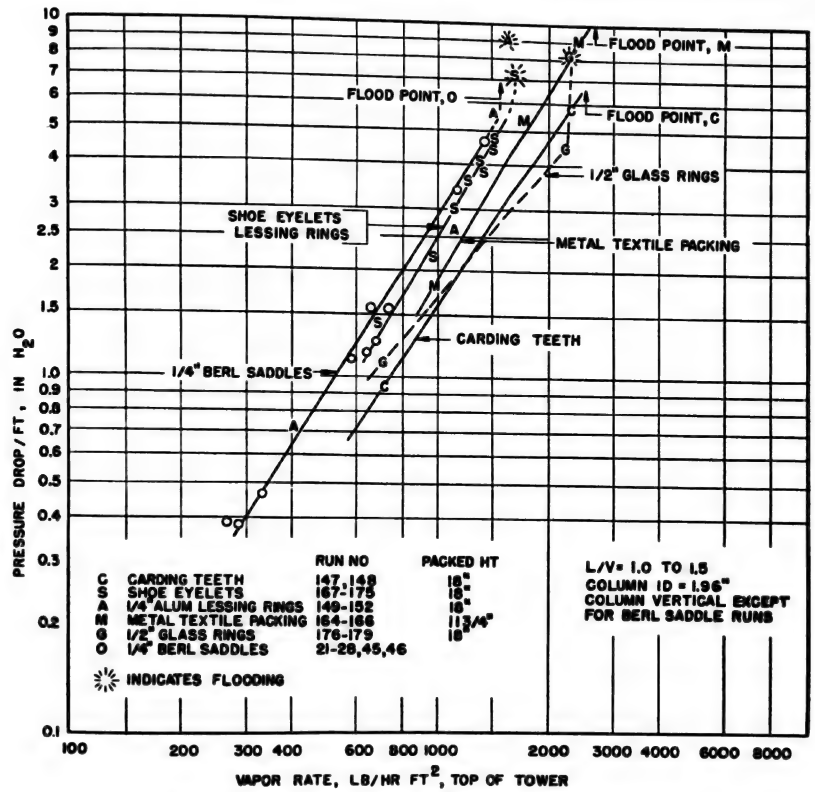


FIGURE 18. Relation between pressure drop and vapor rate for various packings.

which the packing efficiency was adversely affected by increased throughputs. In a vertical tower the HETP of carding teeth was apparently independent of throughput, having a constant value of 7.4 in. The HETP's of the helices varied between 3 in. and 6 in.

Carding teeth have the second highest capacity of all packings tested, 2,520 lb per hr per sq ft of liquid at total reflux. The helices have about the same capacity as ¼-in. Berl saddles, 1,500 lb per hr per sq ft.

Exell Packing. This is a close pitch screen spiral wound around a rod and inserted in a column. The size tested had a ¼-in. core and was fitted in a 1-in. diameter tube. The capacity was so low (350 lb per hr per sq ft) that it was impossible to operate the apparatus. No efficiency data were obtained. Because a packing of such low capacity was of no use, no further tests were made.

Fiberglas. Three different kinds of Fiberglas were tested, one of these at three different packed densities. The tower inclination was not measured. As expected, the lowest density material had the highest

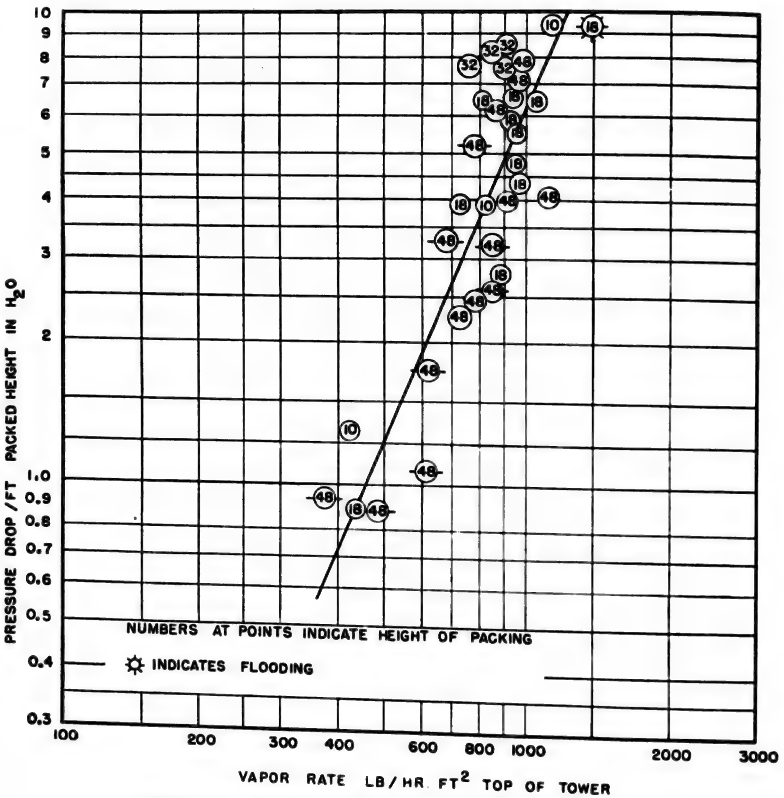


FIGURE 19. Relation between pressure drop and vapor rate for glass rings.

capacity. With Fiberglas No. 1 the capacity dropped from 1,920 to 1,510 lb per hr per sq ft when the density was increased from 0.72 to 1.79 lb per cu ft. The best HETP obtained was 6.9 in.

Haydite. This material is an expanded shale aggregate produced by roasting and grading the natural shale. Haydite is manufactured by the Cooksville Company, Toronto, Canada. The packing may be obtained in various sizes. For the finer material, HETP's of 1.5 to 2.0 in. were reported with benzene-carbon tetrachloride mixtures, and an HETP of 0.8 in. was reported with oxygen isotopes water mixtures.

The two sizes used in the tests were 4 to 8 mesh and ⅜ in. to ½ in. The packed density was 2.5 lb per cu ft and the voids were 55% to 58% of the total volume. These values hold for both size ranges. The surface area estimated by the manufacturer is 1,600 sq ft per cu ft for the smaller size and 280 sq ft per cu ft for the ⅜-in. to ½-in. size.

These tests were made in towers of unknown verticality. The finer size range was retested in a verti-

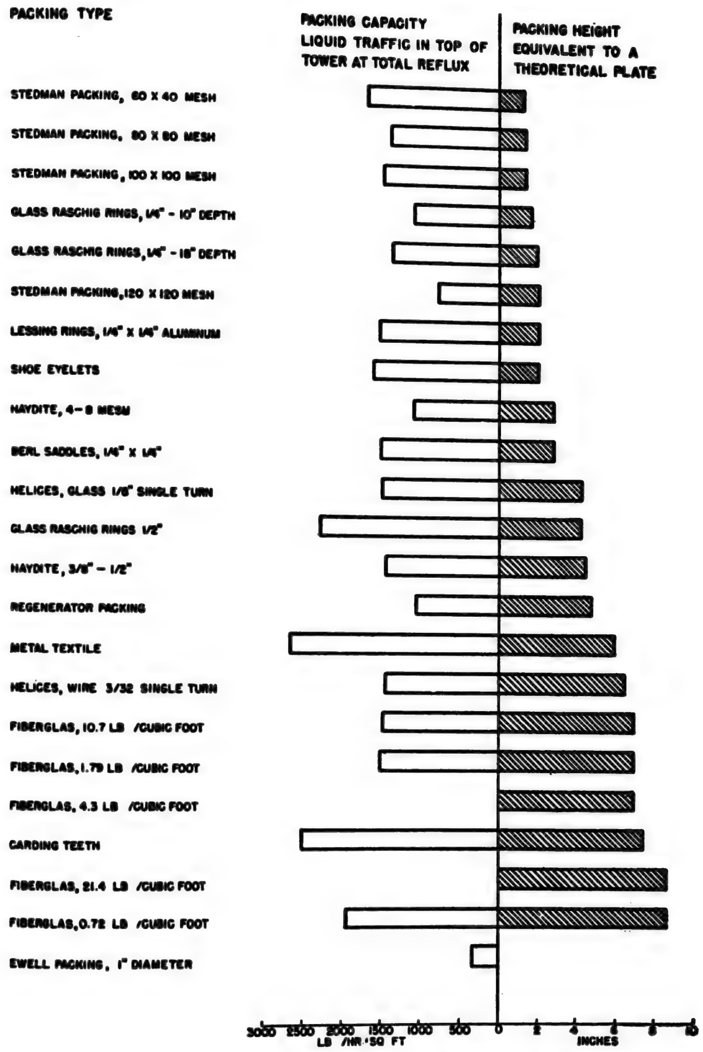


FIGURE 20. Summary of efficiencies and capacities of various packings.

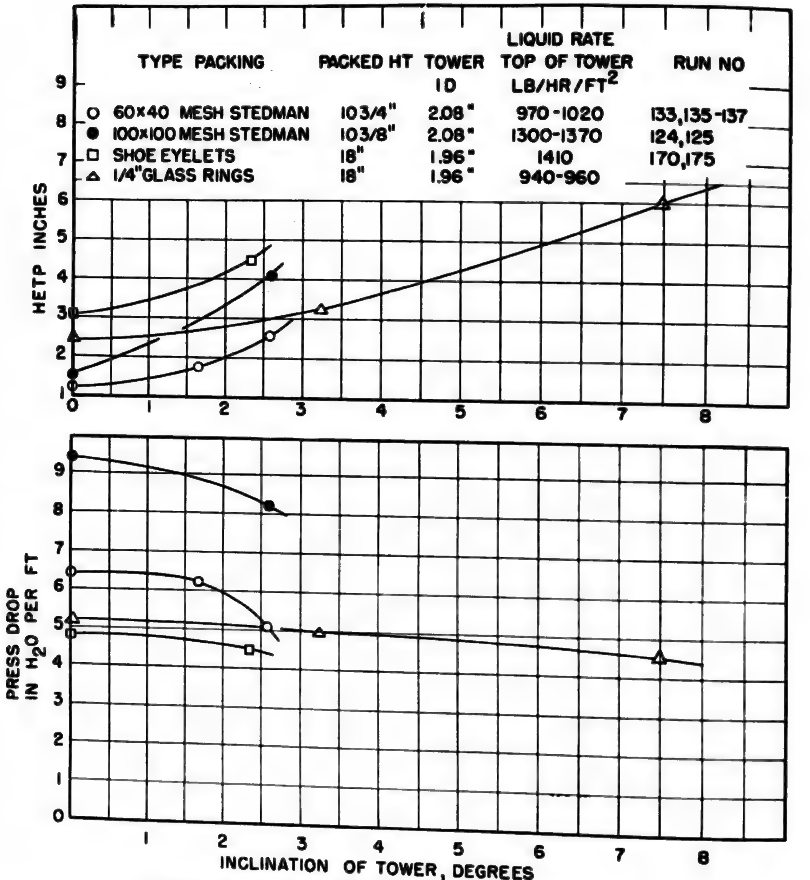


FIGURE 21. Effect of verticality of tower on efficiency and pressure drop.

cal tower. In this latter series of runs the tower was operated above total reflux so that it was not possible to compute the HETP. No capacity measurements were made in the vertical tower.

In the Yale tests 4- to 8-mesh Haydite and 1/4-in. Berl saddles gave about the same efficiency, both having a minimum HETP of 2.7 in. The best HETP of the coarse packing was 4.4 in.

The capacity of the packing may be limited by either actual flooding of the packing or by the lifting velocity of the particles. The particles, being porous, have the apparent specific gravity of 0.7. In the first tests with the 4- to 8-mesh size, one-third of the packing in the tower was blown overhead at a load of 1,250 lb per hr per sq ft. If the lifting velocity is less than the actual flooding velocity, it is necessary to

retain the packing between screens. The actual lifting velocity in liquid air fractionation has not been determined for any size of packing, but in view of the light weight of Haydite it would seem a wise precaution to place some sort of a barrier above it.

FIGURE 22. Various tower packings.

When tested in the Pennsylvania State College tower, the efficiency of the fine packing was about twice that of the 1/4-in. Berl saddles. This may mean either that the performance of Haydite is less influenced by the tower diameter, or that the tests in the small tower are in error because of the unknown inclination. The capacities measured in the two towers are in agreement.

Regenerator Packing. This packing consisted of a 2-in. diameter coil of the crimped aluminum strip used in the regenerative heat exchangers. The strip was 27/32 in. wide with an uncrimped thickness of 0.013 in. The thickness of the crimped strip was 0.045 in., the pitch and angle of crimp were 0.174 in. and 45 degrees respectively. Two strips with the crimping opposed were wound together to make up the coil. The estimated surface area was about 600 sq ft per cu ft, while the packed density was 54 lb per cu ft.

This packing behaves as if it were a bundle of small wetted wall columns, that is, there is no tendency of the packing to redistribute the liquid after the initial distribution.

The tower was tested twice, the first time with unknown verticality. In these tests the lowest HETP was 4.7 in. at the flooding point. The tower was retested in a vertical position, but since it was operated with a high oxygen drawoff it is impossible to compute the HETP. The capacity was not redetermined.

Lessing Rings. This packing is much like a Raschig ring; the only difference is an addition of an axial partition the entire length of the ring. The packing was tested in a vertical tower. The efficiency varied only 30% over a fourfold range of feed rates. The best HETP was 2.0 in. at the flooding rate of 1,550 lb per hr per sq ft at total reflux. This ring system was one of the best packings tested.

Glass 1/4x1/4-in. Raschig Rings. Tests made in a vertical tower with this packing produced some extremely interesting results. Two different depths of packing, 10 in. and 18 in., were used. The results, which are plotted in Figure 15, show the shorter length to be the more efficient and to have the lower capacity. The agreement between the HETP for the two heights is slightly better when plotted as a function of pressure drop than as a function of the liquid or vapor traffic in the top of the tower. The pressure drops per foot of packing at the flooding point were equal, but the capacity of the 10-in. section was only 80% of the capacity of the 18-in. depth. The HETP of 1.6 in. and 1.9 in. at the flooding points were better than those obtained with any other bulk packing.

The differences in the efficiencies may have been the result of either the effect of height upon the liquid distribution, or an actual difference between the nature of the packing in the two tests. The variation in the capacity indicates that possibly the 18-in. depth was more loosely packed. The packed densities were not measured.

Following these peculiar results, further tests were

made with packed depths of 18 in., 32 in. and 48 in. The results are plotted in Figure 23. Because of the effectiveness of these heights it was necessary to use relatively high oxygen drawoffs to avoid the analytical errors arising from extremely high purities obtained at total reflux. Owing to uncertainties in the feed composition, HETP's have not been computed for these runs. Instead, the results are presented in the form of oxygen purity as a function of the drawoff rate.

Figure 23 shows the amazing fact that the 32-in. depth actually performs better than the 48-in. depth, which is 50% longer. Although the shorter section might be expected to be more efficient per unit length than the longer, it certainly does not seem reasonable that additional length could possibly decrease the fractionating ability of a tower. It therefore seems reasonable to assume that the packing in the 32-in. depth was so arranged that it was more effective. This is substantiated by the fact that the pressure drops in the 32-in. section were higher than in the 48-in. column. This should not be taken necessarily to mean that liquid distribution is greatly affected by the packed height.

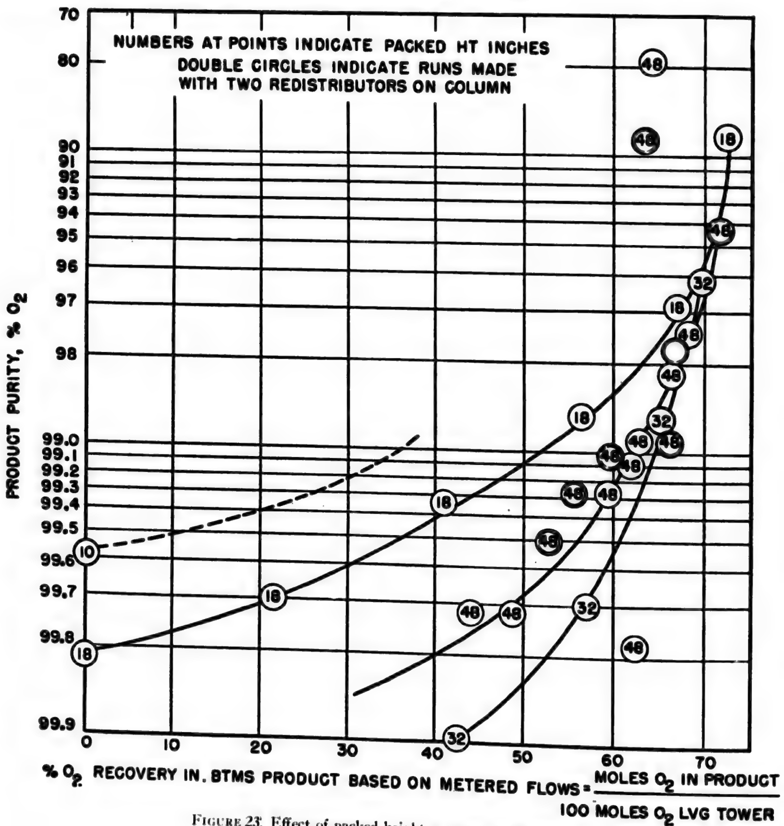


FIGURE 23. Effect of packed height on tower performance.

Distribution of Liquid

Tests were made for liquid redistribution in the 48-in. tower. Two types of redistributors were tested, one which directed the liquid to the center of the tower, and the other type which sent the liquid to the tower wall. Normally, in towers operating above room temperatures, the liquid tends to move toward the wall, but in the case of liquid air it was thought that perhaps heat leak would tend to dry the packing at the walls, and that therefore redistribution should be made toward the outside of the tower. These tests were made in a vacuum-jacketed column in which the heat leak was about half that of the Santocel insulated unit used for the 18-in. tower tests.

The tests with the two distributors are those outlined with the double circle in Figure 23. If there is any effect of these redistributions it is an adverse one.

One-half Inch Size. A few tests were made with this larger size of glass ring packing. The maximum capacity was 2,300 lb per hr per sq ft, but the best HETP was only 4.2 in. The high capacity of these rings relative to the 1/4-in. size suggests that the adverse effect of diameter on HETP might be partially overcome by their use. In other words, it is possible that to do a given job a tower might be as efficient when packed with the larger rings, because the higher capacity would permit a smaller diameter tower to be used.

Shoe Eyelets. The eyelets tested were 5/32 in. long, made of 0.007-in. brass stock, and had a packed density of 55 lb per cu ft. The chief advantage of the packing is that the heat capacity is low compared to that of ceramic rings or saddles. The starting time of a unit is thus decreased by their use.

The eyelets show about the same efficiency as Lessing rings, having a minimum HETP of 2.0 in. The capacity at total reflux is 1,630 lb per hr per sq ft.

Stedman Packing. Two general forms of this material are available, the conical type, made for use in very small laboratory columns, and the triangular pyramid type. Only the latter type has been tested in the research project.

The HETP data are summarized in Figure 24. In the vertical setup, tests were made with four 2.08-in. towers, each differing in the mesh of the screen used. These were 60x40, 80x80, 100x100 and 120x120. The efficiency and capacity decrease with decreasing mesh openings, as shown in Figures 17 and 18. The efficiency of each of these is, within experimental error, substantially independent of the throughput. The first three sizes are very close in performance; the HETP reported varied only from 1.15 in. to 1.45 in., while the finest mesh has an HETP as high as 2 in. In addition, the capacities of the first three range from 1,400 to 1,700 lb per hr per sq ft while the 120x120-mesh size floods at 800 lb per hr per sq ft. Although the superiority is slight, the 60x40-mesh packing is the best.

The larger tower tests showed the importance of completely wetting the packing by a preliminary flooding. Also, it had been suggested that heat leak tended to oppose the wetting by evaporating liquid from the outside of the packing layers. An interesting series of runs were made to show the influence of wetting and heat leak upon performance.[11] A hollow jacket was placed around the column and the 1 1/4-in. annular space between the tower and the jacket was filled with insulation. When filled with air, the jacket acted as a heat leak shield. The insulation between the jacket and the column eliminated excessive heat transfer between the two. The packing was wetted by filling the tower with liquid.

The results of these tests may be summarized as follows.

1. At high feed rates, that is greater than 1,000 lb per (hr) (sq ft) there is no difference between the flooded and shielded, and the flooded but not shielded packings. Without shielding or flooding the HETP is 30% worse.

2. At low feed rates, that is, about 500 lb per (hr) (sq ft), the performance was as given below:

Type of Operation	HETP Inches
Flooding and shielding	1.05
Flooding only	1.15
Shielding only	1.3
Neither flooding nor shielding	1.65

The whole range of HETP variation is only half an inch at the low rates, but this is 50% of the lowest HETP.

These data should not be applied quantitatively to columns of different diameter, because the effect of heat leak should diminish as the tower diameter increases.

Metal Textile Packing. This packing consisted of woven metal cloth rolled into cylinders which were stacked above one another in the tower. The wire diameter was 0.006 in. and the packed density 17 lb per cu ft.

This packing had the highest capacity of any tested [2,600 lb per (hr) (sq ft)], but the HETP of 6 in. is decidedly poor.

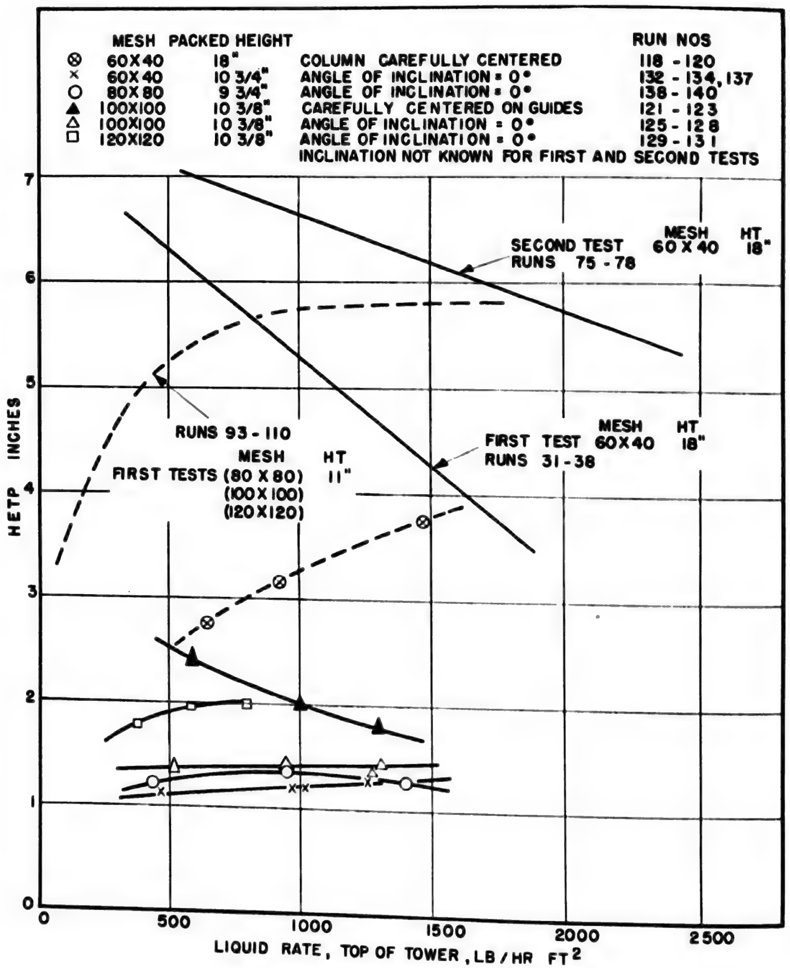


FIGURE 24. Stedman packing performance.

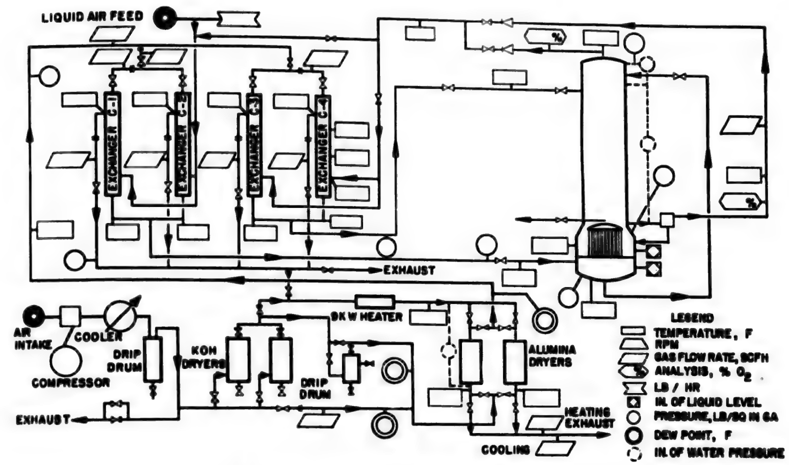


FIGURE 25. Experimental setup for large towers.

8.7.2

Large Column Tests

A flow sheet of the large scale testing equipment is shown in Figure 25. The unit was similar to a low-pressure oxygen plant except for the difference in its source of refrigeration.[11] Here refrigeration was supplied by the injection of liquid air into the exhaust gas side of the heat exchangers. Consequently the control and operation of the tower approximated those of an actual unit.

Berl Saddle Packing

The tower (Figure 26) used with Berl saddles as bulk packing was the first of the full-size towers to be tested. It was designed and built at approximately the same time as the tower for the M-2 unit. The packed height and diameter of the test tower were chosen so that experimental data would be directly applicable to the design of fractionation equipment for the M-2 and other portable units. The tower diameter below the vapor feed point is less than that above in order that the best possible efficiency might be attained in each section by operation at the highest permissible liquid and vapor rates. The first packing to be tested was 1/4-in. Berl saddles, as Yale tests

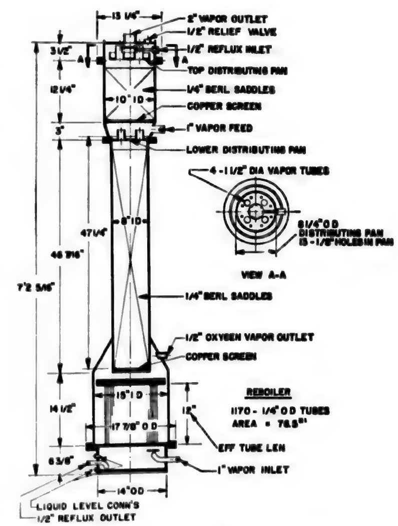


FIGURE 26. Details of packed test tower.

showed this to be the most efficient of those under consideration.

A series of single liquid feed runs at varying throughputs and oxygen production rates were made. The total packed height in these runs was 58 in. Figure 27 illustrates the results, giving the smoothed curves for varying throughputs. As expected, the packing efficiency increases with the feed rate.

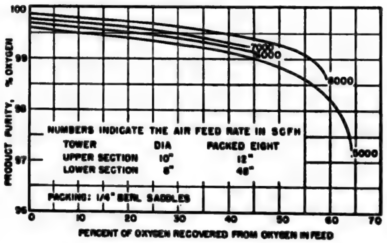


Figure 27. Relation between air feed and oxygen recovery and purity.

In order to obtain good efficiency data, an additional series of runs was made with a constant oxygen recovery of 25% at feed rates from 5,000 cfh to the flood point, which was about 8,500 cfh. The data so obtained show that the HETP varies inversely as the 0.6 power of the feed rate.

The efficiency of the saddles, judged by these runs, was very poor. The best HETP was slightly less than 6 in., or about three times the best value found in the small Yale column. This large, adverse effect of diameter was much worse than had been anticipated. The decreased efficiency was probably caused by poor liquid distribution and the consequent need for redistribution. This is not an easy problem to solve in a short tower. The best redistributors all involve some method of collecting liquid out of contact with the vapor and then redistributing it. Since packing height is sacrificed by this redistribution, it is possible that with the low packed height allowable any increase in efficiency thus gained might be offset by the decreased amount of packing.

Following the single tower experiments, a series of runs was made using the low-pressure vapor feed to increase the oxygen recovery. A summary is shown by the curves in Figure 28. These show startlingly how the simple single tower yield may be raised through the use of vapor feed.

Stedman Packing

Long before the tests with saddles were finished it was evident that a much more efficient tower must be developed if the process specifications for portable units were to be met. Two towers, therefore, were designed, and their construction ordered—a Stedman-packed tower and a tray column.

Published Stedman packing performance with benzene-ethylene-dichloride mixtures showed only a 25% decrease in efficiency in 6-in. diameter packing versus 2-in. diameter packing. On the basis of the small column tests, a 6-in. diameter tower was large enough to be used in portable units. Although in the Yale tests Berl saddles were about twice as efficient as Stedman packing, it appeared that in a larger tower

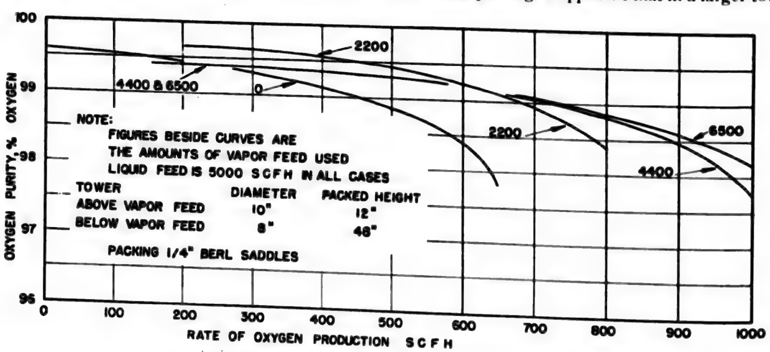


Figure 28. Effect of vapor feed on oxygen recovery and purity.

the latter might be better because of the much smaller effect of diameter. On this basis a tower with a total of 3 ft 9 in. packed space was ordered and tested.

After the first few runs as a single-feed tower it was discovered that if the packing were completely wetted by filling the entire tower with liquid air the efficiency was improved, in fact almost doubled. This peculiarity of Stedman packing has been the subject of a great deal of conjecture. There is a question as to whether or not at any given feed rate the screen might eventually become entirely wetted and the better efficiency thus obtained in the course of normal operation. Conversely, if the tower is flooded with liquid before operation begins, the possibility exists that the packing might become unwetted and the fractionation efficiency impaired. That either or both of these effects occur to some degree is shown by the general erratic performance of Stedman packing.

To call the performance of Stedman packing erratic is not to imply that the material is unsatisfactory. On the contrary, the average HETP of 3 in. for this packing is easily half that of the Berl saddles. Although the deviation from the average is as much as 50%, the maximum HETP is still substantially less than the best value for Berl saddles. This is shown graphically by Figure 29, in which all the single liquid feed runs are given. There seems to be no noticeable

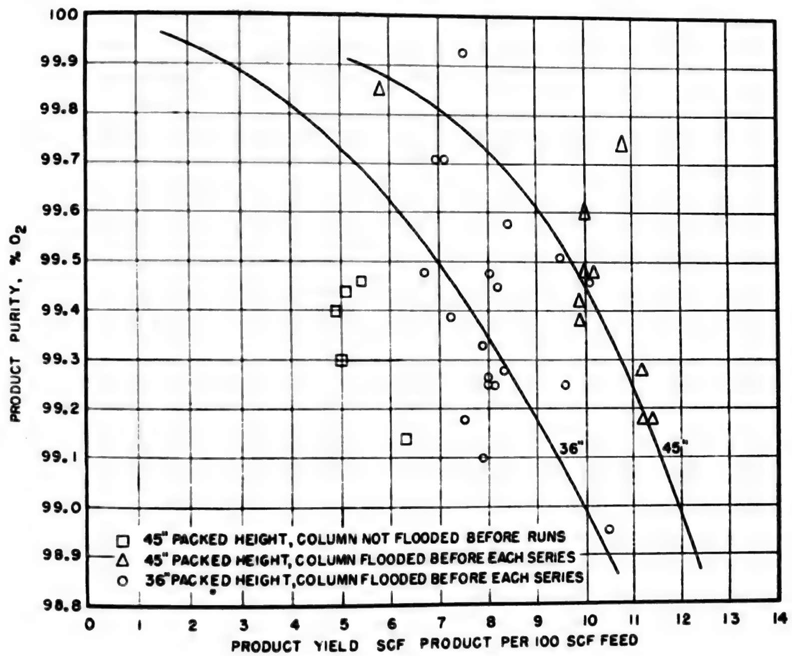


Figure 29. Stedman 6.08-in. diameter tower performance.

effect of feed rate upon the efficiency. This is unlike the behavior of bulk packing. Perhaps the reason for this is that the major effect of increased liquid and vapor loads is to extend the wetted surface of other packings, but since the surface of the Stedman packing is already presumably wetted by preliminary flooding, no further increase in its transfer surface is possible.

The tests that had been made were sufficient to

show that with Stedman packing there was a very good chance of meeting the production requirements of the portable units.

Haydite Packing

The results of a few runs made with 4- to 6-mesh size Haydite packing in the original Pennsylvania State College test tower are shown by Figure 30. At the same liquid and vapor loads the Haydite packing is more efficient than the saddles, but has only 70% of the capacity of ¼-in. saddle packing. The effect of tower diameter appears to be less than in the case of saddles.

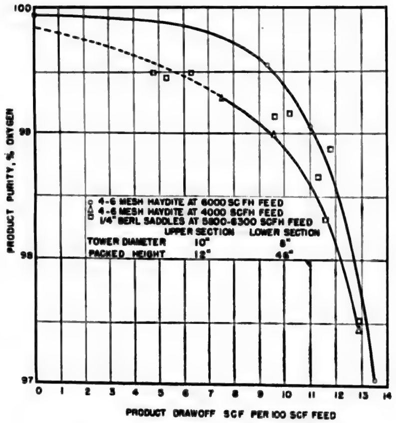


Figure 30. Packed tower performance.

The characteristics of Haydite packing in this mesh size are not good enough to compete with either Stedman packing or tray towers. Other mesh sizes might be tried, but it is likely that smaller size would give greater efficiency with reduced capacity. It is possible that Haydite might be useful in rocking towers and in large columns because of the apparent small effect of diameter.

Tray Towers

Independent Engineering Company Tower. This tower, 12 in. in diameter, composed of 15 sections of two trays each containing a large number of small bubble caps, was purchased from the Independent Engineering Company, O'Fallon, Illinois. The sections were the standard production model used in the mobile units manufactured by Independent.[1]

The purpose of this test was to compare this tray with the tray of entirely different design which was being developed by NDRC. Results with this tower were not so satisfactory as desired for specific NDRC purposes.

M. W. Kellogg Tray Tower. Of all the towers tested in the full-scale size this is the most satisfactory from the standpoint of ease and dependability of operation, as well as efficiency and capacity. The tower is shown in Figure 31 and the trays in Figure 32.

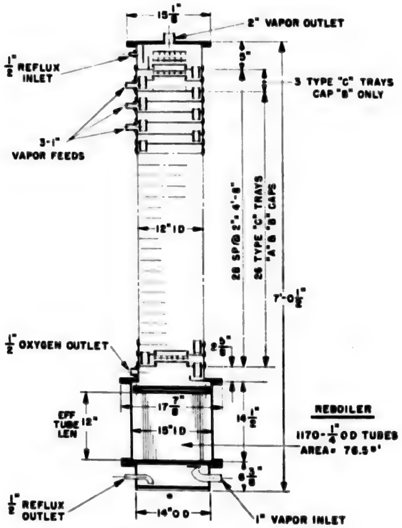


Figure 31. Details of tests in plant tower.

Because there were more *theoretical trays* in this tower than in any other yet tested, the data obtained represent the best appraisal of single-tower and the vapor feed systems. But, because of the high purities and yields, it was impossible to calculate accurately the tray efficiencies.

The effect of the vapor feed location was determined by using each of three inlet nozzles. These were placed below the second, fourth, and sixth trays, and behind the downflow so that the entering

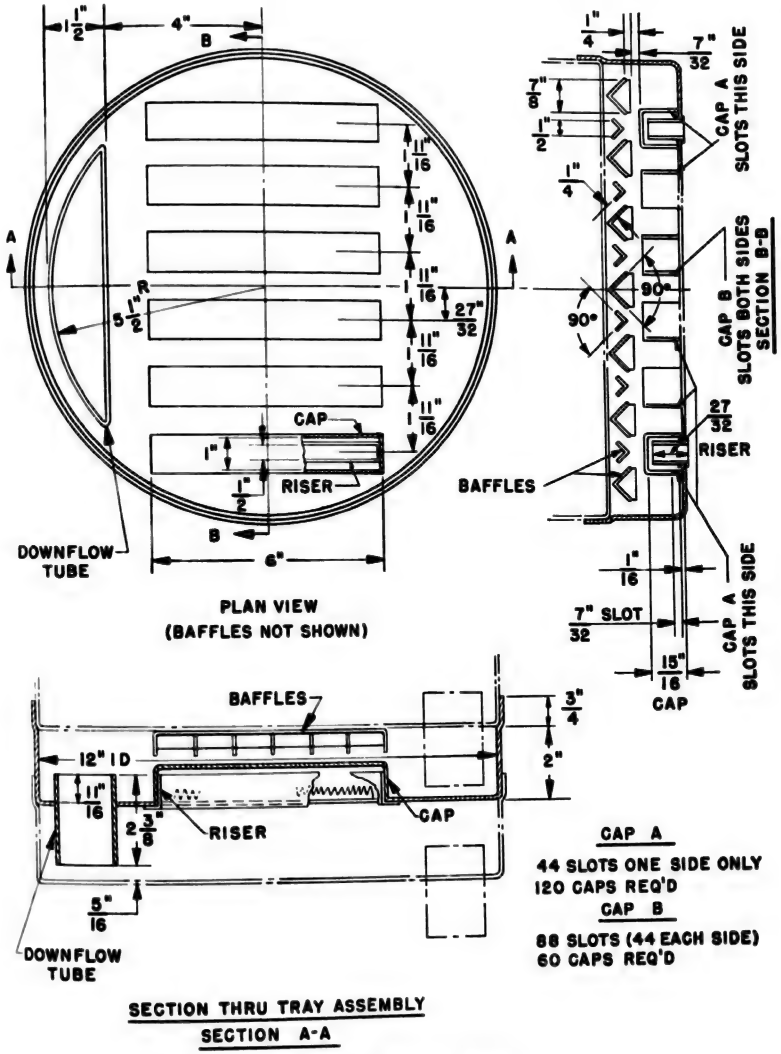


Figure 32. Type C tray details.

vapor would disturb the liquid on the tray as little as possible. The data show that the lowest feed location is the best and the top one the poorest. It is possible that an even lower point of entry would give better performance.

The smoothed performance data are plotted (Figure 33) to show the effect of the relative amount of vapor and liquid feeds upon the oxygen yield for various parameters of oxygen purity. In the graph the data have been represented by straight lines. Those in the upper portion of the chart should curve upwards as the yield approaches zero, and as the ratio *vapor feed/liquid feed* becomes very large.

Short Tray Tower Tests

The success of the tray tower aroused interest in the further development of this sort of fractionation equipment. This involved the accurate measurement of the efficiency and capacity of all trays tested. For this purpose a tower with but four trays was used. When operated at total reflux the uncertainties in equilibrium data exert the least influence, and if the tower is short enough, the product purity is kept in the region in which there is a relatively large composition change over each theoretical tray, thus reducing the error caused by inaccurate product analysis. Another advantage of using total reflux is that

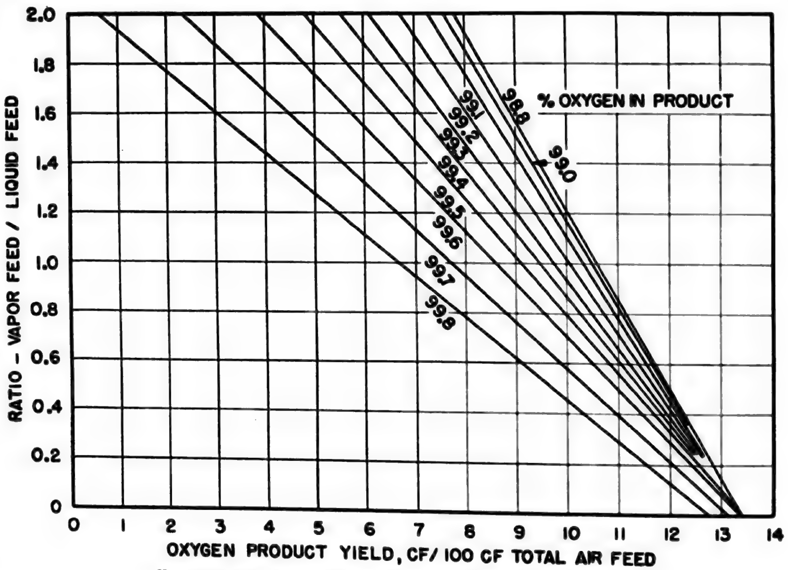


Figure 33. Relation between vapor feed and oxygen purity and yield.

Figure 34 shows the actual data in the form of oxygen yield vs oxygen purity curves for various constant relative quantities of vapor feed. The vapor-feed point was here below the second tray. These curves show the sharp break point that is typical of towers with a large number of trays; that is, the purity is substantially independent of drawoff until a certain drawoff is reached, after which the purity shows an extreme sensitivity to the production.

unknown overhead entrainment does not effect the calculated tray efficiency.

Type C-2 Tray

This is the 2-in. spacing, 12-in. diameter, M. W. Kellogg tray with five cap sides blanked off per tray, used below the vapor feed in the larger test tower. To facilitate construction the shell design was different from the tray shown in Figure 32, but all

dimensions are the same. The tray characteristics may be summarized as follows.

Efficiency. The overall tray efficiency is 84% at a 3,000 scfh feed rate, falls gradually to 75% at a feed of 11,000 scfh and drops sharply to 60% at 12,000 scfh.

Capacity. This seems to be a tray in which the capacity is set by the tray efficiency; even at a feed rate of 13,000 scfh the analysis of the flood point sample line does not indicate flooding. The effective capacity of this tray may be taken as 10,000 to 10,500 scfh, or in terms of the vapor and liquid loads, $Z = 23.5$ at a liquid rate of 95 gal per hr.

Capacity. This is a tray in which the capacity is determined by the flooding point. The overhead entrainment, pressure drop, and the flood point sample analysis all indicate that the capacity is reached at a feed rate of 8,000 scfh. The liquid and vapor loads at this point are $Z = 17$ at a liquid rate of 75 gal per hr. This flooding rate, determined with liquid air, agrees almost exactly with the capacity predicted by the air-water tests on these trays.

West Trays

The tray design, shown in Figure 35, represents an effort to attain higher overall efficiencies through

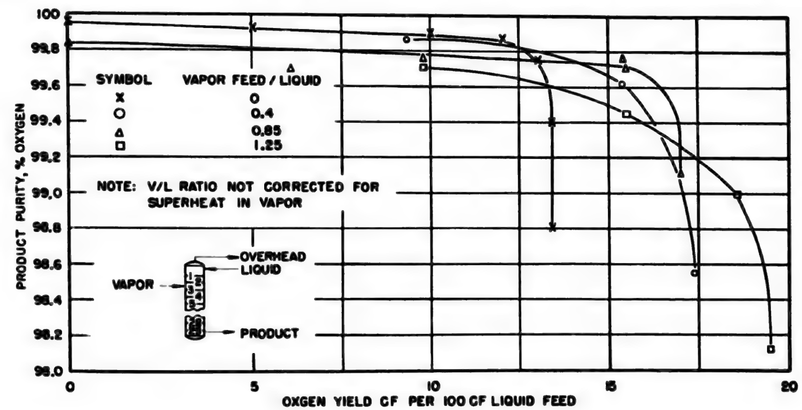


Figure 34. Performance of tray tower.

Type D Tray

The type D tray is similar in design to the type C except that the spacing is 1½ in. The tray was laid out on the drafting board by cutting dimensions wherever possible. After fabrication the trays were tested briefly with air and water to establish the capacity. The characteristics of this tray may be summarized as follows.

Efficiency. The efficiency of the tray is practically independent of the throughput at feed rates of 3,000 scfh and greater. At throughputs lower than this the efficiency falls off because the slots are not all active. The overall efficiency obtained by averaging all the runs is 76%. This is about 5% less than that of the 2-in. spaced tray, but as the tray spacing is 25% less, the net increase in the efficiency of height utilization is 20%.

a cross-flow effect. This cross-flow effect is obtained in a rather unusual way. The plate is divided in half, liquid flows along one side, around a U bend, and back the other side into a slanting downflow which delivers the liquid to the next tray. All the points of liquid entry are in a vertical line. This liquid system has been termed ***co-ordinated reflux***. There is a vertical strip rising from the center of the tray above. The purpose of this strip is to prevent the vapor rising from one side of the tray from mixing with the vapor rising from the other side. Another feature of the tray is the perforated plate lying above the top of the slots of the bubble cap. This is claimed to be important in increasing the efficiency, but the perforated area was found to be too large to be entirely effective in the present application.

In performance the West tray was rather dis-

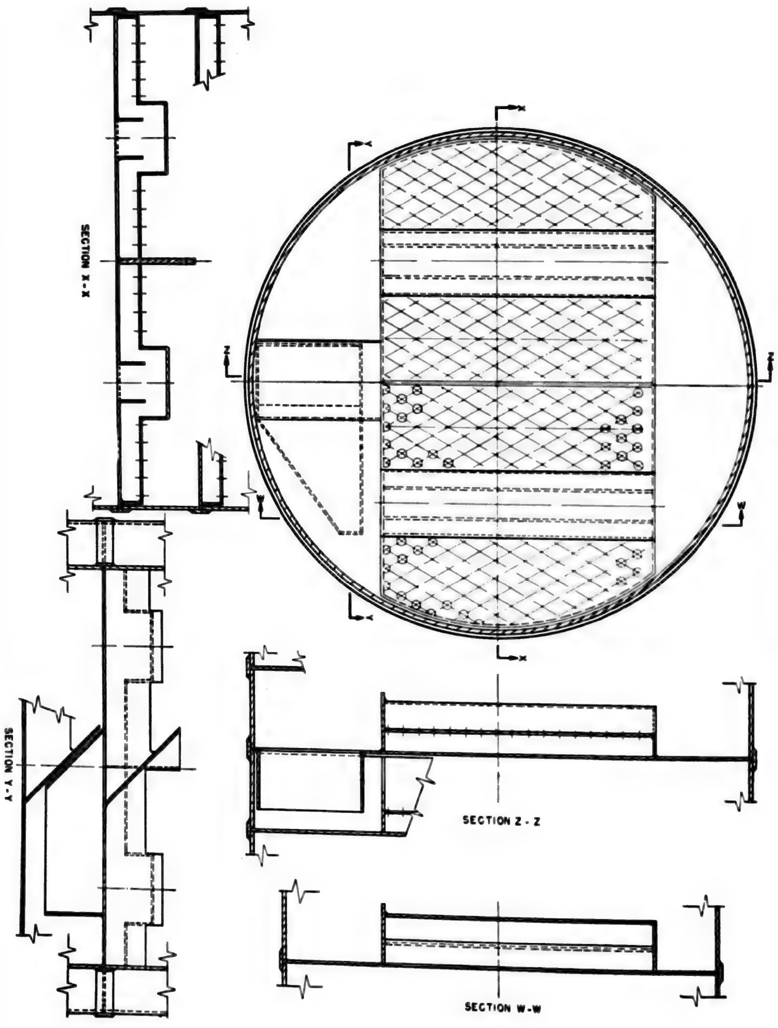


FIGURE 35. Details of West tray.

appointing in view of the favorable theoretical possibilities. It should be noted, however, that because of the complicated construction the perforated plates were warped, and there was a gap between the plates and the shell. There were also other slight deviations from the recommended design dimensions. It is quite possible that the warped perforated plate did inhibit the cross-flow effect. The performance is summarized as follows.

Efficiency. The overall tray efficiency is about the same as that of either the type C or D tray. The value of 78% at a feed rate of 3,000 scfh drops gradually to 72% at 6,000 scfh.

Capacity. As indicated by entrainment and the break in the flood point analysis curve, the tray floods at a feed rate of 6,000 scfh. The reason for the low capacity compared to the type C tray is that in the West tray the liquid path is twice the length and half the width of that in the type C tray. This undoubtedly causes a larger liquid gradient and consequent lower capacity.

As the capacity of the West tray was much less than the type of tray and the efficiencies were about the same, there did not seem to be much point in continuing work on the West tray. However, since there is some doubt that the design was given the best possible tests, and because the co-ordinated reflux principle is a sound attempt to take advantage of the cross-flow effect, further development might be advisable.

8.7.3 Rocking Column Tests

Because of the shipboard applications of fractionation columns, it is necessary to have some knowledge of the behavior of packed and tray towers when subjected to the motion encountered at sea. For such a study the entire test unit was mounted on a platform on which the motion of a ship could be simulated by an ingenious arrangement of cams, rocker arms and gimbals. The unit was so designed that a 5-degree tilt from the vertical was obtainable in one direction and a 15-degree tilt in a direction at right angles to the first. These directions were designated by the terms pitch and roll, respectively.[11,21]

In the pitch direction, the axis of motion was below the tower and perhaps 2 ft away, while the axis of rocking motion passed through the tower somewhat below the midpoint. The form of the pitching and rocking motion has not been described, other than to state the number of cycles per minute and the maximum angle, that is, the variations in the angular velocity throughout a cycle are not reported. An exact description of the tower motion in terms of the three spatial co-ordinates and time is a difficult task. There is probably, however, some optimum location for a tower with respect to the natural axes of a ship.

STEDMAN TOWER

The original 6-in. diameter Stedman tower was the first unit tested under a rocking motion. The experimental work on the new platform included also stationary tests with the tower in both vertical and inclined positions. All tests were made at a constant feed rate of 6,000 scfh. The yield was always 50% or less, to avoid the errors of computing HETP's at high recoveries. Typical results are given in Figure 36, which shows the variation of HETP with column motion.

When vertical and stationary the tower performance fell within the same range reported for the previous tests. When tilted, but stationary, the efficiency dropped badly as had been predicted by the Yale tests. The HETP reached a value of 20 in. for a 5-degree tilt. The tower was so sensitive to the verticality that it was possible to find the perpendicular position by following the oxygen analysis as well as by the use of spirit levels.

To test the symmetry of the unit the tower was inclined in various directions while stationary. Differences in the packing efficiency in the various tilting directions are certainly within the range of reproducibility of Stedman packing efficiency. If there is a real effect of tilting direction, it might be caused by slight non-uniformities in the tower packing itself.

In the rocking experiments only two angles were used, 3½ degrees from the vertical, pitching, and 13 degrees from the vertical, rolling. The influence of motion may be summarized by stating that if the rate of motion is greater than four cycles per minute, there is very little effect of the angle of inclination and the performance is approximately the same as when the tower is vertical or direction active, but is also true when both motions are active, provided that the frequency of either motion is not less than 4 to 5 cycles per minute.

The capacity of the tower was not measured when rocking or when tilted. It might be predicted that the capacity would be less when rocking because of the unsteady pressure drop across the packing. The variation in the pressure drop has been tabulated.

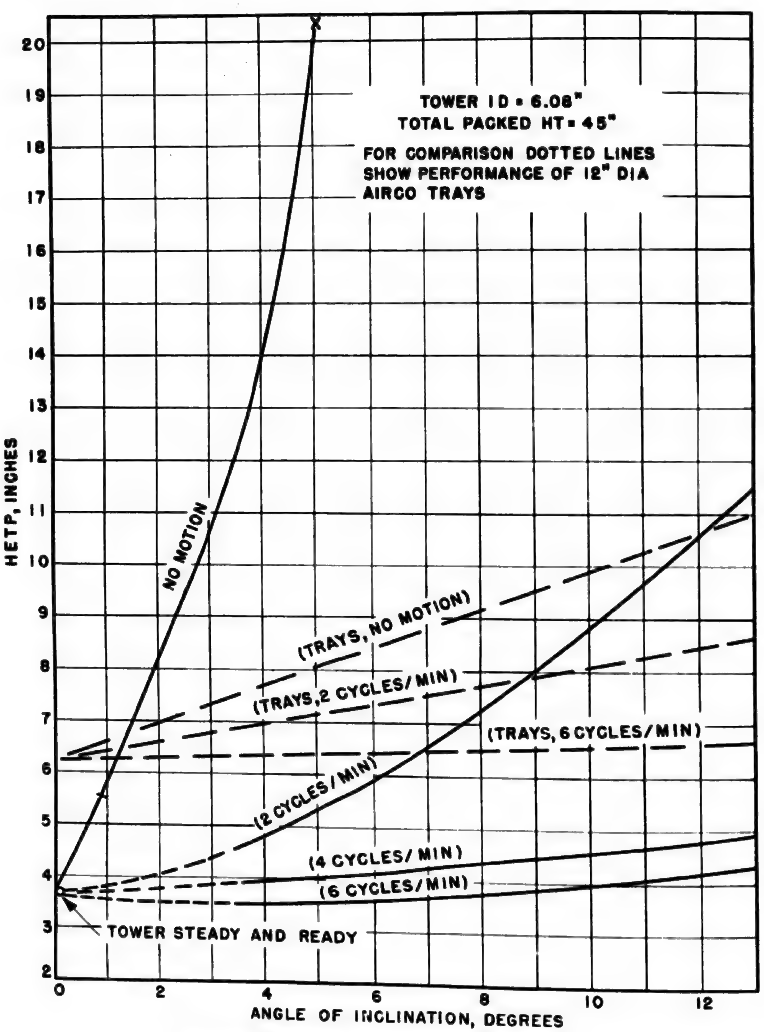


FIGURE 36. Tower performance under rocking conditions.

FOUR 12-IN. DIAMETER AIRCO COMPARTMENT TRAYS

For use in rocking towers the Air Reduction Company proposed a tray which is divided into several compartments, each compartment having its own downflow, sealpot and bubble caps.[23,24] The M-6 unit, which uses these trays, is intended for eventual shipboard service, and because of its size it was impossible to test the performance of the full-size tray when rocking. Therefore, a four-tray test tower with 12-in. diameter trays on a 3½-in. spacing was built and tested. Each tray had fifteen compartments. These compartments are shown in Figure 37.

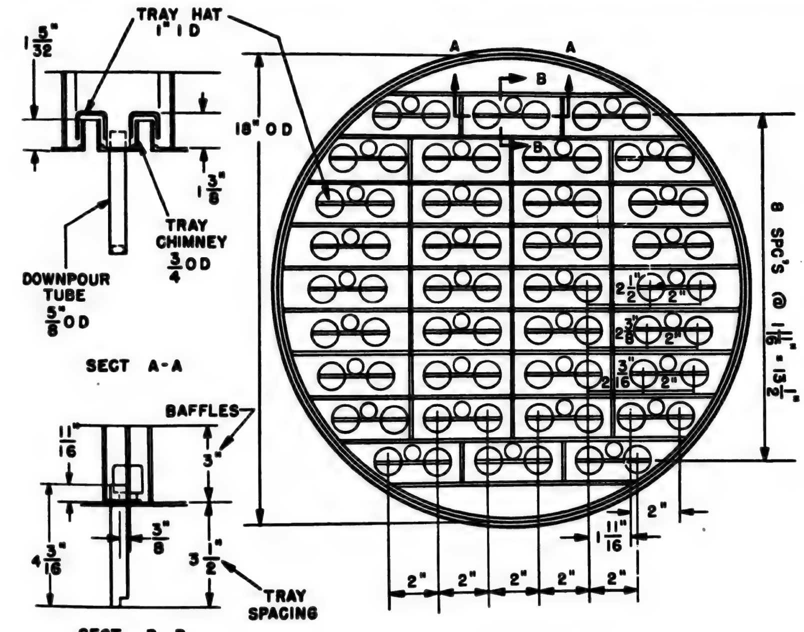


FIGURE 37. Details of compartmented (Airco) tray.

The trays were installed so that the direction of the lesser deflection (pitching) was parallel to the longer side of the compartments. As the tower is essentially a group of parallel columns it is absolutely necessary that the liquid be distributed uniformly among the compartments on the top tray. Therefore, the distributor was designed very carefully and was first tested with air and water before installation in the test tower.

When level and stationary the overall tray efficiency was highest at low feed rate, 70% at 4,000 scfh, falling to 55% at a feed rate of 8,000 scfh, and remaining at this value up to the flooding point. In terms of the liquid and vapor rates the tower flooded at a vapor rate of $Z = 28$ with a liquid rate of 140 gal per hr.[1]

When the tower was rocked the efficiency dropped slightly. No runs were made below an 8,000 scfh feed rate, so it is not known whether the efficiency under motion is higher at lower loads. At feed rates above 8,000 scfh the efficiency was independent of the throughput as in the stationary column. At low angular deflections (pitching), the efficiency dropped

to 50% at 2 cycles per minute, but only to 52% to 54% at 6 cycles per minute. The lowest efficiency encountered was 42% to 45% with a compound motion of two pitch and two roll cycles per minute. In general, lower angles and higher frequencies resulted in the least reductions in efficiency from the stationary, vertical value. No tests were made with the tower inclined but stationary.

The capacity of the trays is about the same when rocked as when vertical. As a throughput of 15,000 scfh entrainment appeared in the overhead gas when the tower was stationary, but when rocking there was no entrainment at this feed rate. The tower pressure dropped, however, indicating a flooding point of about 15,000 scfh either rocking or stationary.

Two 10-in. Diameter Airco Type Trays

These trays are similar to the trays to be used in the M-6 unit above the vapor feed point. Each tray has eight Airco compartments; tray spacing is 6 in. It was necessary to reduce the tower diameter to 10 in. so that the required tower loads might be within the capacity of the test air supply.

Since the purpose of the tests was to reproduce the conditions in the upper part of the M-6 tower, vapor feed was introduced at the bottom of the two-tray section while liquid was fed in the normal manner to the top. No efficiency data were taken since only capacity information was desired.

At the maximum available air supply of 15,000 scfh, entrainment appeared in the overhead when the tower was stationary and level, but disappeared when the tower was rocked. The pressure drop of 1 to 2 in. of water at this point indicated that the tower was not flooded. The loads at the point of entrainment were: vapor rate of $Z = 43$, and liquid rate of 85 gal per hr.

Air Reduction Company Test Towers

The experimental tower tests made by Air Reduction Company were for the purpose of developing towers suitable for shipboard units and portable plants.[22]

The tests made with packed towers were inconclusive because the air rates are greater than the capacity of the tower. The tests with tray towers were part of the necessary groundwork in the development of shipboard columns. The information shows in general only that the efficiency drops 20% to 50% when the trays are rocked. The motion was a rocking one in one direction only and the axis was beneath the tower.

The results of tests made with packed towers are summarized briefly.

Packing	HETP
¼-in. brass Raschig ring	4.0 to 4.5 in.
¼-in. Berl saddles	4.5 to 5.0 in.
½-in. Berl saddles	5.3 to 6.0 in.

These tests led to the installation of a 6-in. ID tower having 24 trays in the Air Reduction Company's portable unit, as it had been found that a 3⅛-in. tray spacing gave an 80% efficiency or an HETP of 3.9 in. The operation of the tray tower was also thought to be more reliable than that of a packed tower.

Experiments with a 14-in. diameter tower, packed with ¼-in. porcelain rings, were made to ascertain if packing could be used in the M-6 unit. The very poor results show the enormous effect of tower diameter on efficiency. The ¼-in. porcelain rings had been used in the small tower and were reported to be "as good as the ¼-in. saddles."

8.7.4 Fractionating Column for Shipboard Operation—the J Tray

In view of the intended application of oxygen units to service on shipboard, it was necessary to develop a highly efficient fractionating tower tray for operation under rocking motion conditions. A tray (Type J)[1,3] was developed, which embodied an attempt at high capacity and high tray efficiency under both rocking and stationary conditions, with a reasonably low tray spacing.

Details of the tray are shown in Figure 38. Essentially the tray is a 3 in. by 9 in. rectangular sheet perforated with ⅛-in. holes. The overflow weir is 2 in. high and a baffle 2 in. high extends across the middle of the tray; these features maintain adequate submergence of the perforations when the tower is tilted. A 1-in. bed of crimped wire cloth is suspended beneath the tray to limit the inter-tray entrainment. A 6-in. tray spacing is used. For a larger column a number of such units would be set side by side in separate compartments. It is intended that the longer axis of each plate be aligned parallel to the length of the ship so that this axis tilts with the less extreme pitching motion and the shorter axis tilts with the rolling motion.[1,21]

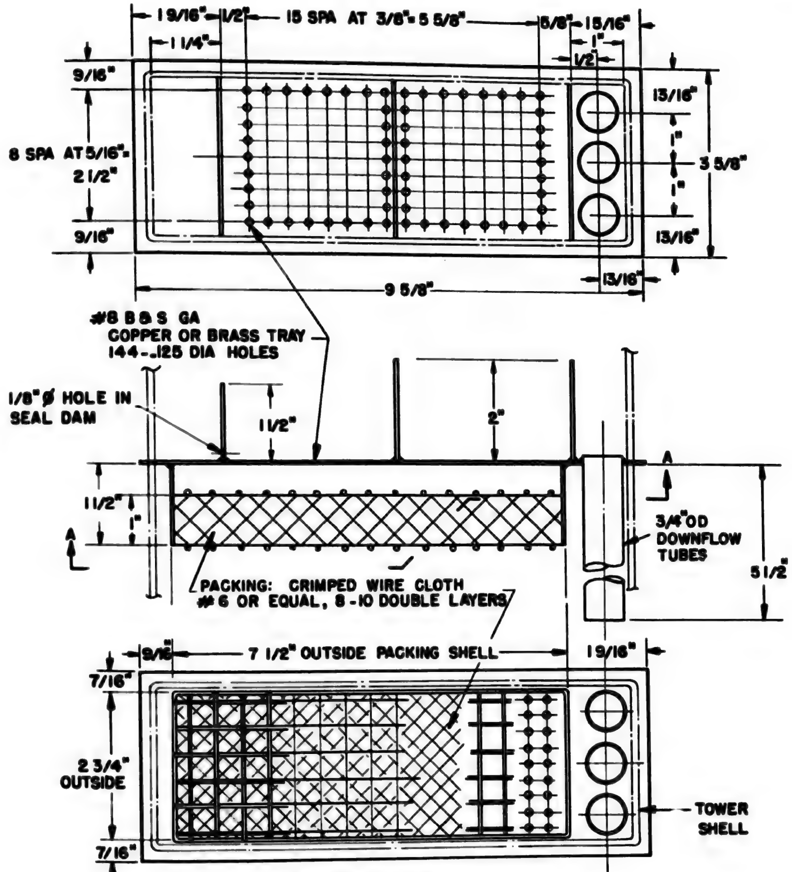


Figure 38. Details of type J trays.

Performance

A small tower consisting of four type J trays was constructed and tested in the rocking platform apparatus.[11,21] The apparatus is similar to a low-pressure oxygen plant, with liquid air as the source of refrigeration. Dried, CO_2-free compressed air at about 100 psi is cooled to liquefaction temperature in a heat exchanger by cold air returning from the fractionating tower and exhausting to the atmosphere. The cold compressed air is then totally condensed in the reboiler at the bottom of the fractionating tower, and the liquid is throttled into the top of the

tower. A small part (10 to 15%) of the liquid vaporizes through the reduction in pressure, and the remaining liquid passes down the tower trays countercurrent to vapors rising from the reboiler.

The gas from the top of the column is passed through a calorimeter in which a measured electric heat input can be maintained, and the rise in temperature of the stream determined. Liquid air for refrigeration requirements is added to this return stream before it enters the exchanger and the exhausts from the system. In addition, any desired quantity of vapor can be by-passed around the tower trays in order to change the liquid-vapor flow ratio through the trays. The entire plant is mounted on a platform which can be rocked with separate or combined pitch and roll motions, with each motion independently variable in frequency and amplitude.

Flooding points were established within limits of about 5%. The tower becomes flooded at a critical vapor load which is independent of liquid load over the range studied. Apparently the downcomers are sufficiently large that there are practically no friction losses due to liquid flow, and if the static pressure drop between two successive trays is lower than the maximum hydrostatic head available to force liquid into the lower tray, adequate liquid flows can be handled. The critical vapor load occurs when the hydrostatic head and the pressure drop are equal, and at higher vapor loads there can be no liquid flow whatsoever.

At a tower pressure of 6 psi, the critical vapor load is 5,700 scfh. This corresponds to a linear velocity of 1.7 fps and a mass velocity of 2,450 lb per hr per sq ft, based on the free cross section of the tower (total area minus downcomer area). The highest liquid-vapor ratio used in the tests was 1/57, which is higher than the usual range of interest in oxygen separation, but probably even considerably higher ratios would not result in appreciable reduction of the critical vapor load.

The average tray efficiency was found to be consistently high over the entire range of liquid feed rates studied. From the lowest feed rate, 2,550 scfh, up to the flooding point, 5,700 scfh, the reboiler vapor analysis was constant at 97% oxygen at total reflux. The number of theoretical plates required for this separation was estimated at 3/7, and thus the average tray efficiency, defined as the ratio of theoretical plates to actual plates, was constant at 93% for the four-tray tower.

Rocking Conditions

Steady-state conditions were achieved at two motions, a pitch of 3½ degrees each side of vertical at a frequency of 5 cycles per minute without roll, and a roll of 15 degrees at 2 cycles without pitch. The tray efficiency and capacity were unaffected by these types of motion. Further runs were made with a 3½-degree, 4-cycle pitch both alone and combined with the 15-degree, 2-cycle roll, and although steady-state conditions were never reached, the results in general showed that the tower performed about the same while rocking as when stationary and vertical.[18,19]

It was concluded that a type J tray tower would function as well on shipboard as in stationary service, and this in addition to the high-tray efficiency and reasonably low-tray spacing made the design appear quite attractive for the M-5 low-pressure liquid oxygen pilot plant for submarine propulsion application. Accordingly a large type J tray tower was constructed and installed in the M-5 unit. This tower consisted of 16 trays each having four adjacent compartments, with the compartments about 25 per cent larger than the single compartment used in the small test tower. Vapors from the four sections can intermix to some extent between trays, but the four liquid streams remain separated.

The column functioned satisfactorily in the unit, although the average tray efficiency was only about 75 per cent, which is considerably lower than the 93 per cent value obtained in the test tower. The reduction was attributed mainly to unequal liquid distribution to the four tower sections.[20]

8.7.5 Other Small-Column Tests

Tests were made on the column of the Keyes unit to evaluate shoe eyelets and the use of a spiral inserted in the column before filling with the eyelets.[5] The screen was supposed to increase the efficiency by providing a longer path for the liquid, but the runs were in the flooding region, and only one point is given for the tower without the spiral. The plain tower probably has more capacity than the tower with the spiral.[1]

8.7.6 Rotary Rectifiers

In an effort to develop a small-size, high-efficiency, high-capacity column for the Collins unit, experiments were made on power-driven rectifiers.[5,25]

These rectifiers consisted essentially of a plain or studded cylinder rotating within a cylindrical shell, with fractionation taking place in the annular space between rotor and case.

The data on benzene-ethylene dichloride fractionation give an indication of the performance of these various rectifiers and permit the following conclusions.[1]

1. The behavior of the rectifiers is unaltered when made to operate in steeply inclined positions, 0 to 37 degrees, except at very low rpm.

2. For small throughputs there exists an optimum rpm above which the rectifying action is decreased, probably due to back-mixing of the vapor. For high throughputs, the vertical vapor velocity in the range of rpm studied is great enough to prevent any appreciable back-mixing. Probably the effect would have been found at sufficiently high speeds.

3. Doubling the clearance between the rotor and the case causes only a slight decrease in rectifying ability and power consumption of the rotor.

4. The power supplied to the rotor increases rapidly as the boil-up rate, or throughput, is increased.

5. The HETP is greatly reduced by putting axial rows of pins in the case. These pins mesh with the studs of the rotor providing better contact and, therefore, increasing the rectifying action of the column. The power requirement of the rotor is increased, but the decrease in HETP makes it possible to operate at lower rpm.

6. At constant rpm there exists an optimum throughput above which the efficiency or number of transfer units, NTU, is decreased. This is, in general, noticeable between 2,000 and 3,000 rpm and 12 to 13 fps superficial velocity. It should be noted that the superficial velocity is based on the total cross-sectional area of the case. In the 6-in. OD column the annular area is only 23½% of the case cross-sectional area.

A rotary shoe-eyelet packed column was used in the final models of the Keyes units but performance data are not yet available. The Badger Company units built for the Navy likewise had rotating columns installed in some cases but final performance data are not available.

Many variations of plate columns were also experimented with and complete details can be found on their performance in the references.[1]

Table 3

Unit*	Feed rate scfh		Oxygen product	
	Liquid	Vapor	Rate scfh	Purity per cent O_2
M-1	6,000	0	1,000	99.5
M-2R	8,000	4,000	1,000	99.5
M-3	2,800	1,950	380	99.0
M-4 Giauque	5,700	0	57 lb/hr	99.5
M-5	31,200	19,000	384 lb/hr	99.5+
M-6	36,500	20,300	453 lb/hr	95.5+
M-7	8,000	4,000	1,150	99.5
			1,300	99.0
M-8	7,000	5,000	1,000	99.0–99.3
M-10 Air Reduction	3,000	0	400	99.2–99.4
M-11 Keyes	4,000	0	36 lb/hr	99.1–99.4
M-12 Little-Latham	4,000	0	14 lb/hr	99.5
M-13 Collins	1,500	0	150	99.5
M-27	8,000	4,000	Same as M-7	
M-31 Le Rouget	6,000	0	54 lb/hr	99.0
E. B. Badger unit	4,500	0	580	99.5
Independent Engrg. Co. unit†	6,250	0	600–800	99.5
M. W. Kellogg-Ft. Belvoir unit	6,250	0	800	99.5

* See Chapters 3 and 4.

† This is not an NDRC development.

8.8 PERFORMANCE OF TOWERS DESIGNED FOR NDRC UNITS

Towers designed for various NDRC units have been tested under operating conditions. Table 3 lists the unit designation and the more pertinent operating or design figures.

Results of operation of these towers are completely summarized in the M. W. Kellogg report.[1] Only a few of the most successful applications will be indicated here.

TABLE 4. Liquid air fractionation performance of the M-7 mobile low-pressure oxygen unit.

						Expander				Product				
Run No.	Date	Length of steady operation hours	Air feed scfh	Vapor feed / Liquid feed	Tower pressure psi	Speed RPM	Suction pressure psi	*Suction temp F	Estimated throughput scfh	Rate scfh	Purity % O_2	Yield scfh per 100 scfh of feed	†Yield from test tray tower for same feed conditions	Test tower yield / Actual yield
15	11/21/43	7	12,050	0.525	12.3	127	87	−247	4,140	60	99.88	0.50	9.0	18.1
15	11/22/43	12	12,000	0.469	10.7	130	80	−241	3,830	1,220	99.4	10.16	11.52	1.14
15	11/23/43	12	12,000	0.585	11.0	143	89	−244	4,430	1,200	99.36	10.0	11.15	1.12
15	11/24/43	3	11,800	0.473	11.0	134	77	−242	3,790	1,200	99.44	10.16	11.45	1.13
15	11/24/43	12	12,130	0.563	10.6	155	80	−249	4,370	1,196	99.35	9.85	11.21	1.14
15	11/25/43	12	12,100	0.531	10.7	145	79	−251	4,200	1,200	99.26	9.92	11.5	1.16
15	11/26/43	12	12,350	0.462	11.0	115	86	−246	3,900	1,210	99.4	9.8	11.55	1.18
15	11/26/43	12	12,200	0.495	11.1	130	83	−246	4,030	1,240	99.37	10.16	11.5	1.13
15	11/27/43	6	12,200	0.497	11.4	132	83	−246	4,040	1,000	99.70	8.2	10.41	1.27
15	11/28/43	12	12,220	0.466	11.3	120	84	−244	3,890	1,004	99.76	8.22	10.2	1.24
15	11/29/43	11	12,150	0.575	11.1	145	87	−245	4,430	1,380	98.59	11.36	11.81	1.04
16	12/11/43	11	11,600	0.605	11.5	142	85	−250	4,370	1,000	99.69	8.62	9.94	1.153
16	12/12/43	12	11,600	0.59	11.0	144	84	−247	4,310	1,350	98.52	11.64	11.8	1.012
16	12/12/43	6	11,100	0.588	11.0	125	86	−247	4,100	1,050	99.38	9.45	11.1	1.175
16	12/13/43	12	11,300	0.597	11.5	131	87	−247	4,220	1,010	99.55	8.94	10.65	1.192
16	12/13/43	12	11,600	0.597	12.0	142	86	−246	4,330	980	99.2	8.45	11.4	1.35
16	12/14/43	12	12,000	0.548	12.1	135	84	−250	4,240	994	99.69	8.28	10.15	1.226
16	12/15/43	7	12,000	0.548	13.0	135	84	−250	4,240	500	99.90	4.16	8.4	2.02
16	12/15/43	6	11,800	0.6075	14.0	145	85	−251	4,450	520	99.52	4.41	10.75	2.44
16	12/15/43	6	11,900	0.653	13.2	150	85	−252	4,700	990	99.57	8.32	10.35	1.245
16	12/17/43	6	12,150	0.642	12.4	168	85	−247	4,750	1,000	99.44	8.24	10.74	1.303
16	12/17/43	12	12,200	0.603	13.0	156	85	−248	4,590	1,000	99.50	8.20	10.77	1.31
16	12/18/43	12	12,500	0.553	13.5	147	85	−249	4,450	990	99.53	7.92	10.91	1.38
16	12/18/43	5	10,500	0.715	12.3	140	85	−251	4,380	1,000	99.56	9.52	10.1	1.061
16	12/19/43	12	11,750	0.55	11.5	135	83	−248	4,160	1,000	99.57	8.51	10.81	1.27
16	12/20/43	6	11,500	0.607	12.0	145	85	−245	4,350	990	99.56	8.6	10.6	1.231
16	12/20/43	12	11,800	0.77	13.0	185	88	−245	5,140	703	99.57	5.95	9.8	1.65
16	12/21/43	5	11,200	0.733	10.9	170	84	−246	4,740	1,000	99.39	8.93	10.5	1.175
16	12/21/43	12	11,800	0.675	12.2	163	86	−249	4,750	990	99.34	8.40	10.82	1.29
16	12/22/43	10	12,100	0.682	13.0	167	86	−251	4,910	1,020	99.35	8.42	10.8	1.285
17	12/27/43	3	11,900	0.54	10.75	143	80	−250	4,200	1,250	99.25	10.5	11.3	1.08
17	12/27–28/43	9	11,900	0.64	11.0	132	82	−250	4,740	1,100	99.7	9.23	9.2	0.995
17	12/28/43	6	12,000	0.52	11.5	138	80	−250	4,120	990	99.68	8.25	10.0	1.21
17	12/29/43	12	11,900	0.52	11.6	137	80	−250	4,080	1,000	99.73	8.4	9.8	1.17
17	12/29/43	9	11,700	0.63	11.0	169	76	−253	4,500	990	99.62	8.46	10.2	1.21
17	12/30/43	12	11,700	0.62	11.1	169	75	−253	4,450	1,000	99.65	8.55	10.1	1.18
17	12/30/43	6	11,800	0.50	9.4	150	70	−252	3,920	990	99.39	8.4	11.4	1.36
17	12/31/43	6	10,800	0.60	9.2	160	70	−252	4,040	980	99.39	9.06	11.0	1.21
17	12/31/43	6	10,800	0.66	9.0	177	70	−253	4,300	990	99.40	9.16	10.8	1.18
17	12/31/43	6	12,200	0.60	11.0	175	75	−252	4,520	1,000	99.7	8.18	9.86	1.21
18	1/ 4/44	4½	12,000	0.523	10.0	150	76		4,120	1,290	97.8	10.75	12.1	1.125
18	1/ 4/44	6	12,000	0.523	10.2	150	76		4,120	1,300	97.9	10.82	12.05	1.11
18	1/ 5/44	6	12,000	0.509	9.9	145	76		4,050	1,190	99.0	9.9	11.9	1.20
18	1/12/44	10	11,200	2.62	11.0	350	90		8,100	300	99.78	2.68		
19	1/30/44	6	12,000	0.563	12.3	139	85		4,330	1,000	99.61	8.34	10.55	1.27
19	1/31/44	12	12,000	0.555	12.1	136	85		4,290	1,110	99.59	9.25	10.71	1.16
19	1/31/44	6	12,000	0.555	12.3	139	84		4,290	1,200	99.58	10.00	10.75	1.08
19	1/31/44	6	12,000	0.554	12.5	136	85		4,280	1,200	99.30	10.00	11.35	1.14
[illegible]	[illegible]	[illegible]	[illegible]	0.54	12.5	135	86		4,280	1,200	99.32	9.84	11.35	1.15
[illegible]	[illegible]	3	11,800	0.582	12.0	140	85		4,340	1,300	98.80	11.0	11.75	1.07
19	2/ 3/44	4	11,900	0.698	11.8	200	76		4,900	1,050	99.51	8.83	10.34	1.17
19	2/ 3/44	7	12,000	0.618	12.4	150	86		4,590	1,050	99.78	8.75	9.2	1.05
20	2/ 5/44	6	12,000	1.12	13.0	250	87		6,340	990	99.65	8.25	7.5	0.91
22	2/16/44	12	12,000	0.73	12.2	163	92		5,060	1,020	99.84	8.5	8.0	0.94
22	2/16/44	12	12,000	0.675	12.2	168	85		4,840	1,010	99.74	8.41	9.1	1.08
22	2/17/44	12	11,000	0.686	11.1	153	83		4,480	1,110	99.64	10.08	9.8	0.972
22	2/17/44	12	12,000	0.686	13.0	168	86		4,880	1,220	99.63	10.16	9.82	0.966
22	2/18/44	12	13,000	0.561	14.0	150	87		4,630	1,320	99.48	10.16	11.01	1.08
22	2/18/44	12	14,000	0.522	16.0	150	91		4,800	1,400	98.64	10.0	11.98	1.20
22	2/19/44	12	14,000	0.545	16.4	150	94		4,940	1,400	99.25	10.0	11.49	1.15
22	2/19/44	9	14,000	0.560	16.2	155	94		5,030	1,400	98.20	10.0	11.96	1.20
22	2/20/44	12	14,000	0.548	16.1	150	94		4,950	1,400	99.10	10.0	11.7	1.17
22	2/20/44	12	15,000	0.534	18.2	155	98		5,220	1,500	98.75	10.0	11.9	1.19
22	2/21/44	12	12,000	0.66	13.0	156	88		4,770	2,000	76.0	16.7		
22	2/21/44	12	12,000	0.65	12.7	156	87		4,730	2,000	76.5	16.7		
22	2/22/44	12	12,000	0.666	13.4	157	88		4,800	2,000	76.0	16.7		
22	2/22/44	12	12,000	0.666	14.2	155	89		4,800	2,000	80.0	16.7		
22	2/23/44	12	12,000	0.624	14.2	153	89		4,750	2,000	80.0	16.7		
22	2/23/44	12	12,000	0.615	14.1	151	89		4,700	2,000	80.0	16.7		
22	2/24/44	6	12,000	0.630	14.0	152	87		4,640	2,000	78.5	16.7		

* Suction temperature not measured after Run No. 17.
† Based on tests with 29-tray tower at The Pennsylvania State College.

8.8.1 The Kellogg Tray Tower for the M-7 Unit

The most successful large tower for low-pressure work was the one built for the M-7 unit and the Clark production models. This tower, Figure 39, had trays similar to Figure 40. It is difficult to divorce the column performance from that of the unit as a whole; therefore the data are summarized in Table 4 for the unit as a whole. Figure 41 illustrates the characteristics of the column itself.

The oxygen purity is shown as a function of the production rate and the percentage yield. These data show that the unit with this tower easily meets the design specifications of 1,000 scfh of 99.5% oxygen from a minimum air feed of 11,300 scfh. The shape of the production curve shows nothing unusual as it is the same type as that obtained with the test tower.

From time to time it has been suggested that the Stedman tower rather than the tray tower should be used in the mobile units. Proponents of this idea point out that the starting time of a unit is a very important quality, and that 50% to 60% of the M-7 starting time is used in merely filling the trays with liquid. In the case of Stedman packing, the tower is ready for some sort of fractionation as soon as liquid is introduced and reboiling has begun.

Although it is true that a Stedman column is ready for operation with a very small amount of liquid, the efficiency of the tower under these conditions is poor.

The starting time of a packed column unit is less than that of a tray tower by the time required to fill the trays with liquid, but the packing does not reach its peak efficiency until it too has some liquid holdup. The quantity of the holdup and, therefore, the time required to reach peak efficiency is dependent upon the liquid and vapor loads of the tower. On the other hand, a tray tower will produce nothing until the trays are full, but once this point is reached the oxygen recovery in a given height is greater than that for the large packed towers tested. In addition, the performance of the tray tower is much more dependable and reproducible.

8.8.2 Fort Belvoir Unit

The title given to this unit is somewhat misleading as the connection with Fort Belvoir is not obvious. The Engineer Board had expressed some dissatisfaction with the performance for their specific purposes of the early Independent Engineering units. After the successful tests on the Kellogg 29-tray tower

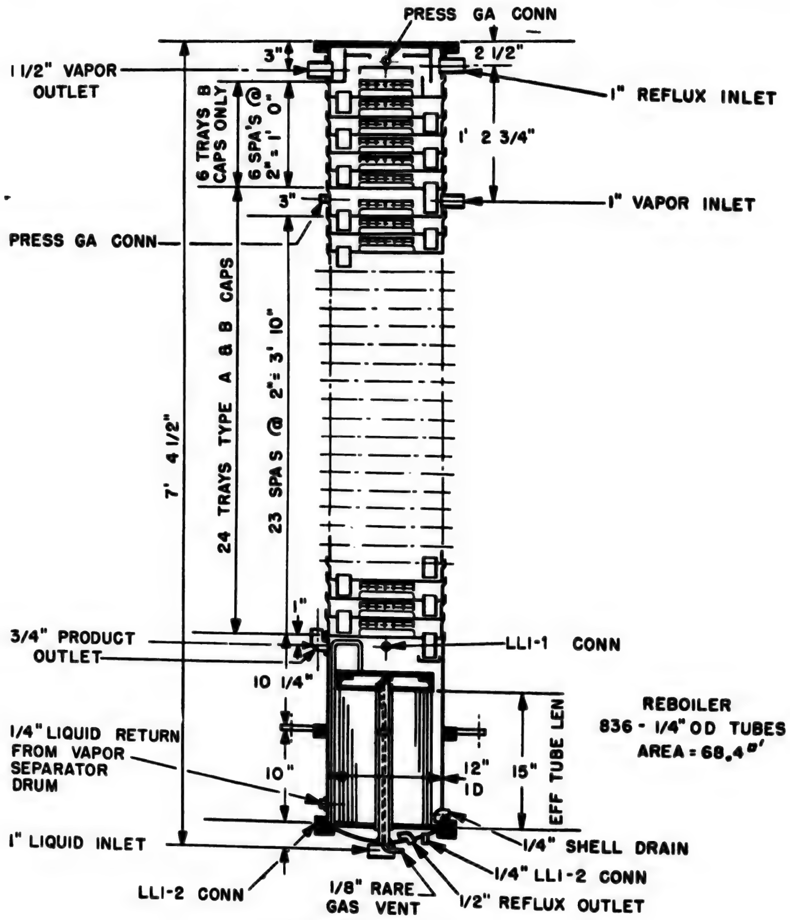


Figure 39. M-7 fractionating tower.

and the unsuccessful test on the Independent Engineering Company tower at Pennsylvania State College, it was suggested that a Kellogg tower be installed by NDRC in an Independent unit at Fort Belvoir, Virginia. Later, through the co-operation of the Independent Engineering Company, the NDRC tower was installed and tested at the Independent plant at O'Fallon, Illinois. The name, "Fort Belvoir Unit," has remained although the tower has not been at Fort Belvoir.

This column was similar to that shown in Figure 39 and it operated successfully. Largely as a result

of these tests the column arrangement of the units built for the Engineer Corps and the Army Air Forces by the Independent Engineering Company was modified and simplified and the production improved.

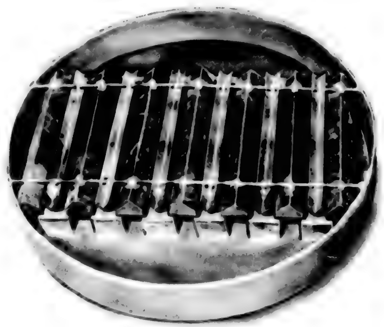


Figure 40. Type C tray similar to those used in the M-7 tower.

8.8.3 Giauque Unit (M-4)

This mobile unit was designed to produce 1,000 scfh of oxygen as liquid.[7] The Linde cycle with a cascade refrigeration system using butane and ethane was originally contemplated. However, Freon-12 was later substituted as a single refrigerant. The tower system (Figure 1) has the provision for nitrogen recirculation which raises the recovery of oxygen from the high-pressure air feed. Because of the difficulty in obtaining an oil-free nitrogen compressor, the recirculation system has not yet been used and the unit has been operated only with the ordinary single-feed fractionating system.

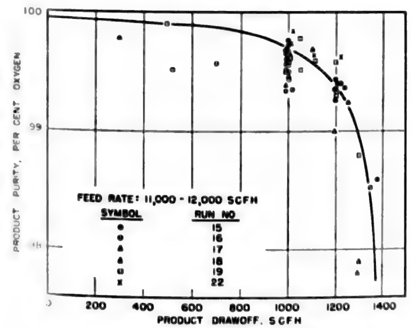


Figure 41. Performance of the M-7 portable oxygen

The tower is 12-in. in diameter and has thirty trays on a 2-in. spacing. Each tray has 85 bubble caps, triangularly spaced. In the development of the tower a test apparatus was used in which the tray action with air and liquid air could be observed visually.

The production of the unit is:

Air feed	5,700 scfh
Oxygen production	60 lb per hr (700 scfh) of liquid
Oxygen purity	99.67%

8.8.4 Air Reduction Company Mobile Unit

This is a high-pressure, Freon-forecooled, single-tower unit. The reboiler is of the coiled type so that the reflux is subcooled to approximately the temperature of boiling oxygen. A description of the tower follows.

Diameter	6 in.	Bubble caps:	
Overall height	8 ft	Number per tray	12
Number of trays	24	Spacing	1⅜ in. centers
Tray spacing	3⅛ in.	Diameter	1 in.
Downflow pipe		Height	1 in.
½ in. diameter (1 per tray)		Riser diameter	½ in.

The following tower performance has been obtained.

Air feed scfh	Oxygen scfh	Oxygen $\%O_2$	No. theoretical trays	Overall tray efficiency	HETP inches
3,000	390	99.2–99.4	...	...	...
2,950	370	99.54	22	92	3.4
2,400	300	99.3	19	79	4
2,400	240	99.7	15.5	65	4.8

Column pressure = 11 psi

These figures, while showing the performance of the unit, do not represent data for tray efficiency calculations. However, considering the highest efficiency given, the HETP is 35% greater than that obtainable with a Kellogg tray at a 2-in. spacing.

8.8.5 E. B. Badger Unit

The E. B. Badger Company built high-pressure units (see Chapter 4) for the United States Navy, using a rotating column packed with ¼-in. by ¼-in. McMahon wire gauze saddles. The performance of

the unit is described in part by the Badger Company as follows.

We have tabulated a series of 26 runs made between December 23 and February 19 and obtained extremely unsatisfactory and inconsistent results. Probably the most important results are the following: The highest purity at the highest yields were obtained with rather low throughputs. This would indicate that the efficiency of the packing certainly did not increase as the throughput increased. The results with the column not rotating are scattered through the results with the column rotating, indicating that there is not enough difference between the rotating and non-rotating vertical column to show up in such inconsistent data.

The object of the runs on this rotating column was never primarily to obtain data on the column, but to develop a practical unit that would meet the requirements of the Navy. For this reason, we do not believe that any good purpose would be served in submitting detailed data on the runs. The use of such data by itself could only cause trouble.

If we now had to give a guess as to the most likely figures to use for the performance of this 4.7 in. diameter column with 36 in. packing, rotating or non-rotating, and with a head in which the unliquefied material was separated above the packing, we would say that it lay close to 99.5% purity and 14.3% by weight yield on the net air charged at capacities running between 63 and 76 cfm of charge air. The results appear to be slightly better when the column was inclined up to 10 degrees and rotated.

The data from one performance are tabulated below.

saddles, the third size (¼-in.) much better than Berl saddles, and each weighs less than one-third as much. Their heat capacity is about one-tenth as great. The maximum throughput of the screen saddles is more than twice as great as the ceramic ones.

The performance data are summarized in Figure 42 for the column shown in Figure 43.

8.8.7 M-5 Low-Pressure Unit

The first column designed for this unit was of Stedman packing and arranged as shown in Figure 44.

Results on operation of the tower were disappointing[16,17] and the tower was replaced by one made of J trays (see section 8.7.4). The J tray tower layout is shown in Figure 12. The design rates for the tower are

Liquid feed	2,389 lb per hr (31,200 scfh)
Vapor feed	1,453 lb per hr (19,000 scfh)
Oxygen product	384 lb per hr (4,500 scfh)
Oxygen purity	95.5% or better

8.8.8 M-6 Medium-Pressure Unit

This is a medium-pressure unit with high-level and low-level expansion engines. Consequently, it was

TABLE 5

Feed rate scfh	Oxygen Product scfh	Purity Per cent O_2	Yield scf per 100 scf liquid feed	Number of theoretical plates	Packed height inches	HETP, inches	
3,750	520	98.6	13.9	..	47	....	Tower rotating at 18 rpm
3,720	450	99.85	12.1	26	36	1.38	
4,400	575	97.45	13.1	11	36	3.3	
3,800	490	99.5	12.9	27	36	1.33	Estimated best tower performance
4,500	580	99.5	12.7	27	36	1.33	

8.8.6 Collins-McMahon Unit

This is a lightweight, compact unit originally intended for operation in aircraft.[25] Air compressed to 150 psi, after heat exchange and expansion through an engine, is condensed in the reboiler and fed to a single tower as liquid feed.

Aside from the unit itself two contributions have been made to the fractionation program. These are the introduction of the differential reboiler and the wire gauze saddles.

Wire gauze saddles made from 100-mesh wire cloth have been used. The second size (⅜-in. square of cloth before forming) performs as well as Berl

possible to use the vapor feed type of tower. The tower, shown on Figure 45, was originally designed to be packed with either ¼-in. Berl saddles or rings but trays were finally used. See Figure 37.

The tower description and design loads are as follows.

Tower	
Total trays	27
Above vapor feed	2 to 5$\frac{15}{16}$ in. spacing
Below vapor feed	25 to 3½ in. spacing
Liquid feed	2,791 lb per hr (36,500 scfh)
Vapor feed	1,567 lb per hr (20,300 scfh)
Oxygen produced	453 lb per hr (5,350 scfh)
Oxygen purity	95.5 per cent or better

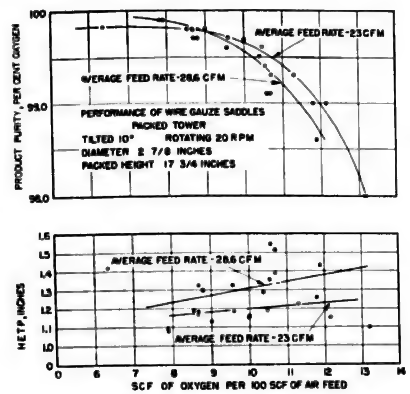


FIGURE 42. Performance of a tower packed with wire gauze saddles.

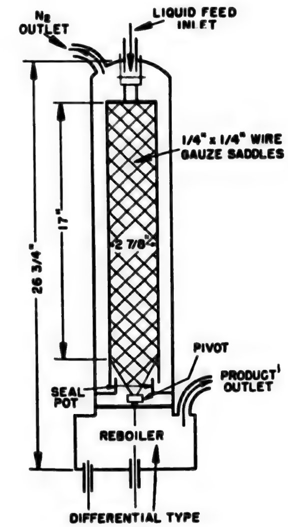


FIGURE 43. Collins unit tower.

8.9 AIR-WATER TESTING OF TRAYS

The technique of air-water testing has proved invaluable in the development of trays for efficient oxygen production.[1,8] The procedure is merely that of duplicating the normal liquid and vapor flows in a tower, measuring rates of flow and entrainment, and making visual observation of the effects. The materials are used at room temperature and pressure to allow easy operation and almost complete visual observation of the tray behavior.

One essential difference between packing and trays as a fractionation device is the extreme complexity of the design of tray towers as compared to packed towers. In the case of trays the efficiency and capacity are sometimes such obscure functions of the mechanical factors that tray design is still an art rather than a science. An added complication is that trays do not necessarily conform to the theory of models. A design which is satisfactory in one size of tower must often be entirely altered if the diameter of the tower is changed.

Some of the factors which must be considered in designing a tray are: tray spacing; tray area; riser area; downflow area; slot area and dimensions; number, type, and arrangement of bubble caps; slot submergence; liquid gradient; and entrainment.

If tray towers are to compete with packed towers it is necessary to use a tray spacing of about 2 in. At such a low spacing the elements of design become very important in the performance of a tray.

The design of trays with this very low spacing appears to be a subject which has not received much attention by the oxygen industry. For instance, the Air Reduction Company stated that the efficiency of height utilization is the same for 3-in. as for 4-in. tray spacing; over 4 in. the HETP increases simply because of the extra spacing. Between 4 in. and 3 in. the entrainment offsets the decreased spacing, whereas below 3 in. the entrainment is high enough to counter the reduced spacing and the result is flooding of the trays and a greatly increased HETP. Another example is the Independent Engineering Company tray which had a low capacity. These two instances suggested that in designing a low-spacing, high-capacity tray the principal problem is the removal of inter-tray entrainment. To do this requires the use of entrainment separators and a tray layout which minimizes splashing.

In the process of development, a few trays were fabricated according to a tentative design and the air-

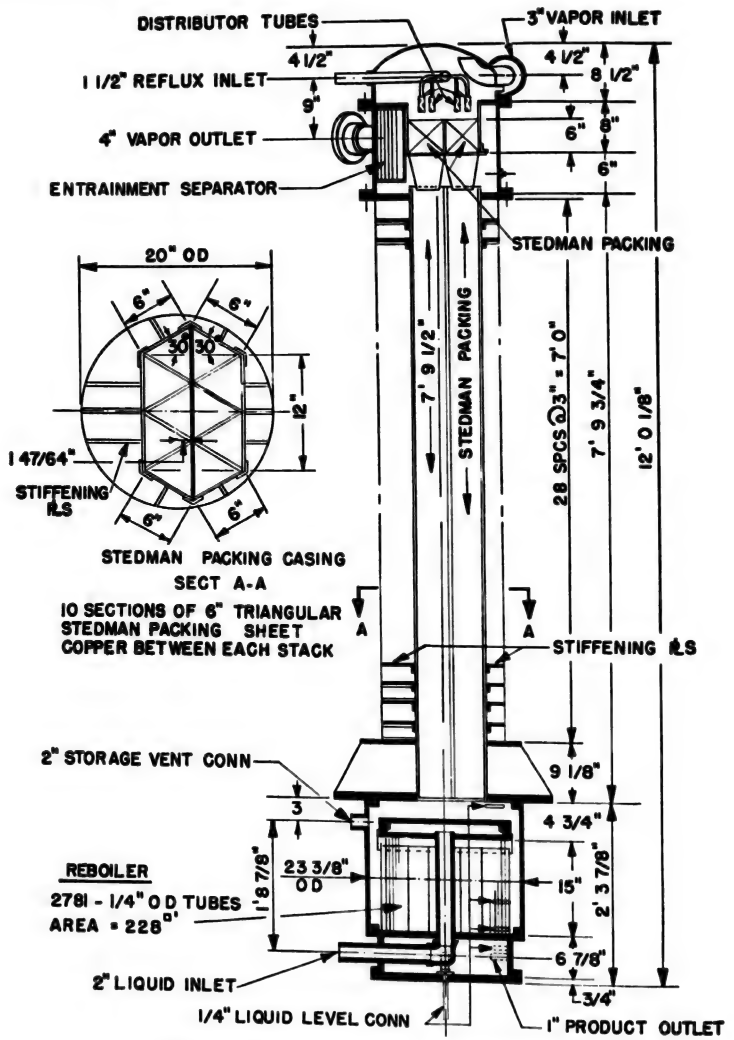


FIGURE 44. Stedman fractionating tower for M-5 unit.

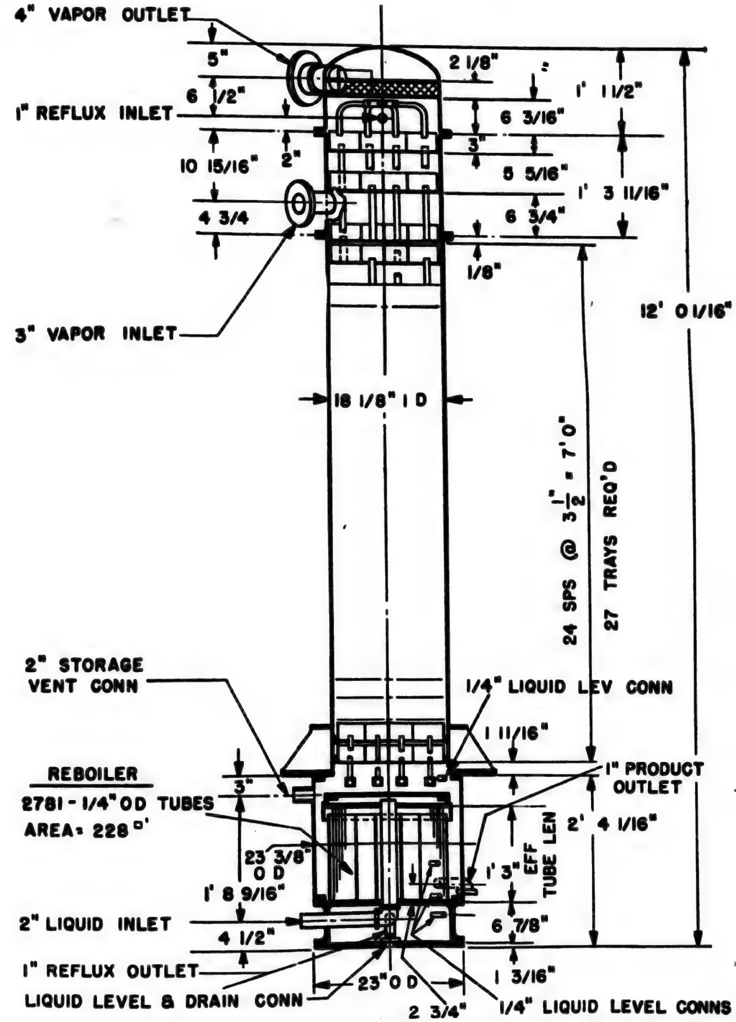


FIGURE 45. Fractionating tower (compartmented trays) for M-6 unit.

TABLE 6. Tray characteristics and areas

Type	M. W. Kellogg Company design trays								Air Reduction Company compartmented tray			Aluminium Plant and Vessel Co.
	A	C-1	C-2	D	E†	F†	J	K	34 Compts.	15 Compts.	8 Compts.	
Number of caps	6	6	6	6	3	2	0	1	68	30	16	2
Tray spacing, in.	2	2	2	1½	3	1½	6	6	3½ & 6	3½	6	2
Tower, in.	12	12	12	12	7⅛	7⅛	3 x 9	3 x 9	18	12	9½	12
Tower area, sq ft	0.785	0.785	0.785	0.785	0.277	0.277	0.187	0.187	1.60‖	0.705‖	0.375‖	0.785
Downflow area, sq ft	0.0865	0.054	0.054	0.054	0.0131	0.0038	0.0077‡	0.0077‡	0.0573	0.0253	0.0135	0.0304
Weir length, in., straight	9	7.4	7.4	7.4	3	2.8	3	1¾	....	....	....	2.94
Weir length, in., curved	....	8.2	8.2	8.2	3.5	....	....	....	59.3	26.2	14.0	....
Riser area, sq ft	0.1225	0.1225	0.1225	0.1225	0.0371	0.0360	....	0.0243	0.185	0.081	0.0431	0.079
Riser area, % tower area	15.6	15.6	15.6	15.6	13.4	13.0	....	13.0	11.5‖	11.5‖	11.5‖	9.94
Between top of riser and cap, sq ft	0.0938	0.0938	0.055	0.055	0.045	0.0315	....	0.030	0.252	0.111	0.0590	0.1015
Between top of riser and cap, % tower area	11.9	11.9	7.0	740	16	11.4	....	16.0	15.7‖	15.7‖	15.7‖	12.95
Between side of riser and cap, sq ft	0.107	0.107	0.063	0.064	0.0341	0.0283	....	0.0243	0.162	0.0712	0.0380	0.0677
Between side of riser and cap, % tower area	13.6	13.6	8.0	8.1	12	10.2	....	13.0	10.1‖	10.1‖	10.1‖	8.63
Slot area, sq ft	0.0502	0.0502	0.030	0.030	0.016	0.0110	0.0123*	0.0125*	0.117	0.0515	0.0274	0.0987*
Slot area, % tower area	6.4	6.4	3.8	3.8	5.8	4.0	6.55	6.67	7.30‖	7.30‖	7.30‖	12.57
Area under teeth, sq ft	0.0306	0.0306	0.018	0.018	0.018	0.0094	....	0.0364§	0.273	0.120	0.0638	0.0903§
Area under teeth, % tower area	3.9	3.9	2.3	2.3	6.5	3.4	....	19.48	17.0‖	17.0‖	17.0‖	11.5§
Weir height above tray, in.	11/16	11/16	11/16	9/16	¾	½	2	1½	11/16	11/16	11/16	1⅛
Submergence to top of slot, no flow, in.	0.406	0.406	0.406	0.280	0.41	0.17	2	¾	0.281	0.281	0.281	19/32
Slotted length of cap, in./tray	72	72	42	42	21	14.5		....	180	79	42	....
Detail drawing No.	M.W.K. 19-A	M.W.K. 87-A	M.W.K. 87-A	(M.W.K. (87-A, (105-A, (117-A	M.W.K. 126-B	M.W.K. 125-B	M.W.K. 164-B	M.W.K. 165-B	Airco R-971-B	M.W.K. 121-G	M.W.K 124-G	(M.W.K. (102-G (90-A (89-A
Figure No.	150	68	68	70	163	164	175	176	153	153	153	75

* "Slot Area" consists of holes in perforated plate.
† Minimum areas permitted by tolerances.
‡ Area in tubes. (Top downflow area = 0.208 sq ft.)
§ Area at outlet of cap under perforated plate.
‖ Tower area for Airco trays assumed to equal area of 4 in. x 1 11/16 in. compartments, that is tower area, sq ft = (No. of compts.) x (4 x 1 11/16)/144.

water tests made with these. With the aid of some sheet celluloid and metal and some ordinary adhesive tape, a great many trial-and-error tests were made before the final design was established. The investigation was concerned particularly with entrainment removal, equal distribution of liquid in the bubbling channels, and the uniform activity of all slots. In other words, although the tray efficiency cannot be obtained with the air-water tests, all the factors which affect the efficiency can be considered.

In addition to the qualitative observation of the behavior, the following variables were measured quantitatively: liquid level in downflow, height of liquid over the downflow weir, liquid gradient across the tray, froth height, pressure drop, liquid and vapor quantities, and entrainment.

At least two trays are required for air-water tests. If only one is used, the entrainment cannot be measured, and in addition a tray exerts a considerable influence upon the pattern of vapor flowing from the tray beneath.

In order to apply the air-water capacity data to other systems, the liquid rate in gallons per hour at flooding is plotted against the flooding gas velocity. The superficial vapor velocity is taken as Z. When used in this manner, the air-water capacity data agree almost exactly with the liquid air data.

All tray types except the A and B trays were developed by the air-water procedure. The Type B trays were not used in any units but became the Type C after testing. Type A trays, used in the M-1 unit, were tested only in the completed tower. For a complete description of the technique of air-water testing see reference.[1]

In addition to the Types C, D, E, F, J, and K trays and the West tray, an exhaustive study was made with the Independent Engineering Company tray to discover the reason for its poor test performance. The characteristics of all these trays are given in Table 6.

8.10 DIFFERENTIAL REBOILER

The idea of utilizing progressive or differential vaporization of the boiling liquid in a tower was first utilized in the Collins-McMahon unit.

A schematic representation on the McCabe-Thiele diagram of differential distillation and the performance of a perfect differential process are shown by Figure 46.

The enrichment obtained by a perfect differential vaporization process in air fractionation is a function of the tower yield and the composition of the liquid entering the vaporizer.

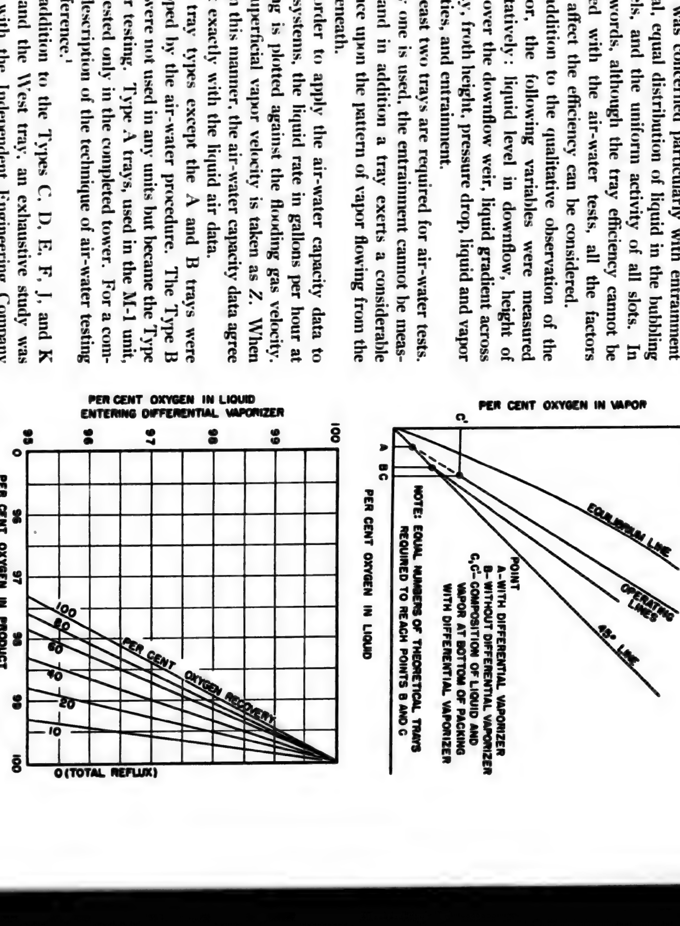


FIGURE 46. Analysis of differential vaporizer performance.

There are two general types of progressive vaporizers.[1] The first is the straight simple or differential distillation in which the vapor is removed as it is formed. The Collins-McMahon reboiler is an example of this type. A perfect vaporizer is one with an infinite length of heat transfer surface.

The second is one in which the vapor passes back over the liquid path. This type should give better results than the first kind, because at any point the vapors returning are leaner in the contaminant than the mixture which would be in equilibrium with the

liquid. This means that there will be some oxygen concentration in the liquid through mass transfer between the phases, in addition to the enrichment resulting from the progressive vaporization.

The coiled type of reboiler used in the Collins-McMahon unit requires more cubic space per unit of reboiler surface than the tubular bundle type, although the coil seems vastly superior in differential vaporization. For this reason and because construction was under way when the idea was proposed, the coiled type reboiler was not used in the units designed by the M. W. Kellogg Company.

Since use of a differential reboiler offers the opportunity of improving the product purity and of lowering the height of a tower, the subject is worth further study. The data available on performance of progressive vaporizers are open to criticism, the M-3 because of its uncertainty, and the Collins-McMahon data because of its incompleteness. Future study should involve the analysis of all streams entering and leaving the boiler.

8.11 SUMMARY

It is believed that the data obtained in this program should be valuable in the design and construction of any liquid air fractionation system by enabling—(1) the estimation of the theoretical trays required for any system, (2) the design of any packed tower through accurate knowledge of the efficiency and capacity of many packing materials, (3) the design of a tray tower using the trays developed by the Kellogg Company and the performance data on these trays, and (4) the use of expansion engine exhaust air to increase the oxygen recovery of low-pressure plants. The data which have been obtained and are essential to the actual design of towers are presented in the following section.

8.12 CALCULATION OF THEORETICAL TRAY REQUIREMENTS

A chart (Figure 4) has been presented, which gives the number of theoretical plates required to make any required oxygen recovery and purity in simple single columns. In the design of a different type of column, the necessary number of theoretical trays may be obtained by rigorous tray-to-tray methods of heat and material balances, and equilibrium calculations. The atmospheric pressure vapor-liquid equilibrium constants to be used are given in Table 1. Further experimental equilibrium data at elevated pressure will extend the scope of tray-to-tray calculations.

Given the required number of theoretical trays and the quantity of liquid air to be treated, it is possible to select a packing or a tray and to set the required size of the tower. Conversely, if the tower size is fixed by other considerations it is possible to determine the oxygen recovery and purity, and the amount of air which must be handled.

The choice between trays and packing will depend upon a number of factors which may vary from unit to unit. For instance, if a short starting time is required, then a medium having a low refrigeration load is indicated. This might be a metallic packing, such as shoe eyelets, with low liquid holdup and low heat capacity. On the other hand, if stability of operation were the prime consideration then a tray tower would be the proper choice.

8.13 PACKING MATERIALS

The efficiency and capacity of all the packings tested in the 2-in. column are given in Table 2 and Figures 15 and 16. Of all those tested, the shoe eyelets, glass rings, Lessing rings and the Stedman packing seem to be the best. The gauze saddles developed by Collins-McMahon apparently perform favorably, but the data available are meager.

The HETP values should be used with caution when applied to large diameter towers. It may be that the decrease in efficiency is entirely the result of poor liquid distribution. This may be overcome by proper initial distribution, followed by successive redistributions. However, it is impossible to predict the performance of such devices.

Figure 47 shows the HETP for various trays and packed towers plotted as a function of oxygen recovery. The fact that the efficiency of the short tray towers is independent of oxygen recovery indicates that the variation in the HETP of the taller packed towers may be fictitious. An explanation of this is that the oxygen purity was low enough in the short tray towers so that the effect of analytical error was minimized. Therefore, it might not be too unreasonable a procedure to use the lower values of HETP in tower design. However, a safer procedure would be to use the actual performance data, such as shown in Figure 48.

To determine the diameter of a tower the capacity of the various packings listed in Table 2 should be

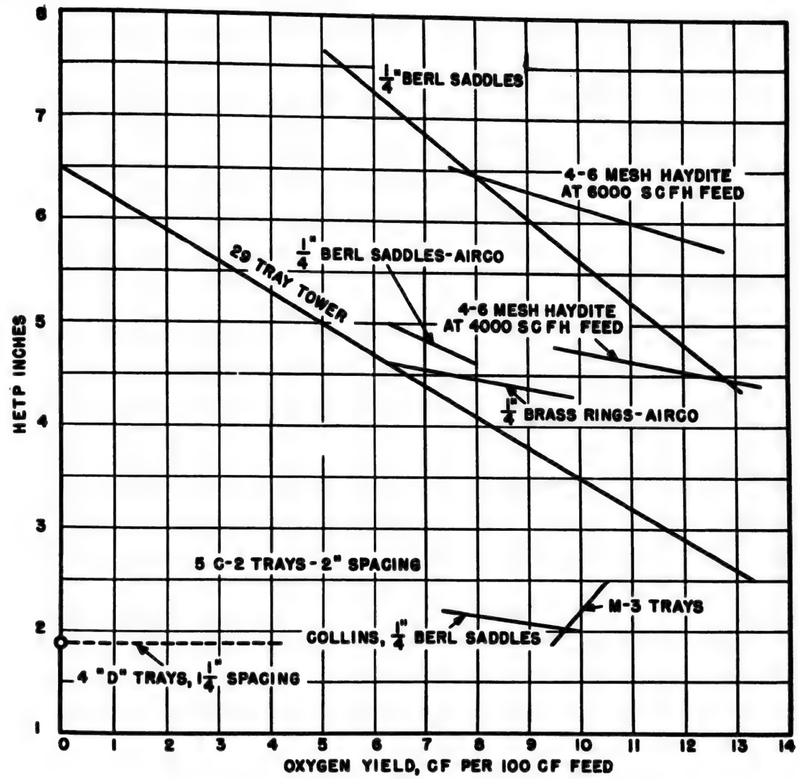


Figure 47. Relation between yield and efficiency for various columns.

used. In correcting the flooding point to pressures other than atmospheric, the flooding vapor load may be taken as approximately proportional to the square root of the absolute pressure. A correlation, available in the literature,[24] relating the flooding loads in packing to the properties of the liquid, vapor, and packing, satisfactorily fits most reported data for other systems. However, when applied to liquid air, this correlation predicts flooding velocities which vary from 30% to 70% of the observed values. Therefore, flooding points for untested packing must be obtained experimentally.

8.14 TRAYS

Nine different trays have been developed for various purposes by the application of air-water testing. This relatively simple technique has proved to be most reliable in predicting the capacity of trays and reasonably accurate in estimating entrainment. The liquid and vapor capacities for all trays tested are given on Figure 49. Owing to the nature of trays, these data should be used only as a guide for any other diameter tray or type of design. Efficiencies of all the trays are in the range of 75% to 80%.

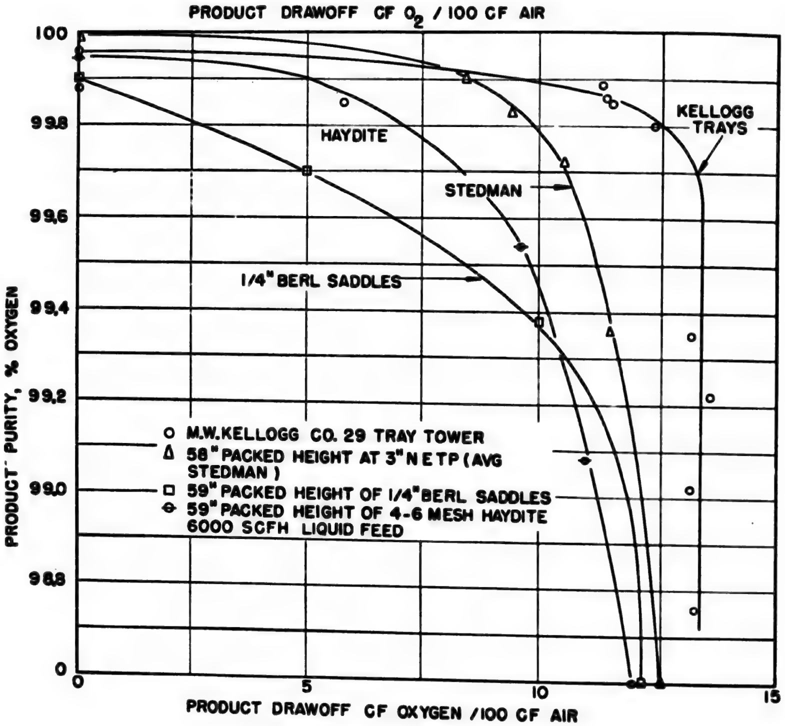


FIGURE 48. Large column performances.

8.15

USE OF VAPOR FEED

In some low-pressure units using a Claude type refrigeration cycle, the air exhausted from the expansion engine at too low a pressure to be condensed, may be used as vapor feed to a single liquid feed tower. The successful use of this scheme in the Kellogg test tray tower is shown by Figure 33. This chart is fairly indicative of the increase in oxygen recovery which may be expected from any reasonably well designed tower using this system. Figure 50 shows the oxygen recovery based upon a constant total amount of air for three cases: (1) all the air is fed as liquid reflux to the tower, (2) a fraction of the air is expanded and sent to the tower as vapor feed, and (3) the same fraction of the air is expanded but is not used in the tower system.

This plot shows that with a single tower, the oxygen recovery may be greatly increased by use of the vapor feed, and that for a fixed air supply it is advantageous to keep the quantity of air expanded as low as possible.

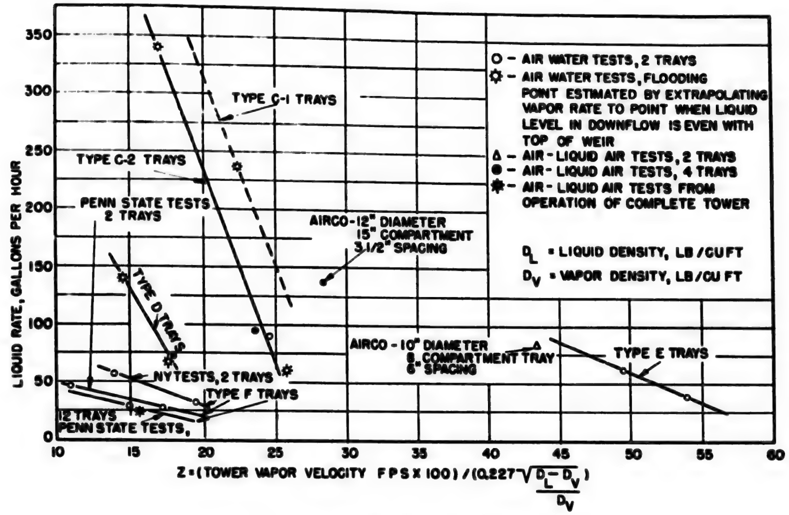


FIGURE 49. Capacities of tray columns.

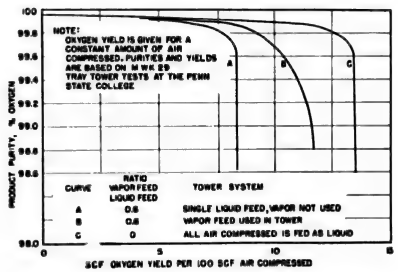


FIGURE 50. Effect of feed on oxygen purity and yield.

Chapter 9

AIR PURIFICATION

By *J. H. Rushton*

9.1 INTRODUCTION

THREE constituents of ordinary atmospheric air must be removed for air liquefaction processes or for the conditioning of submarine air. These substances are water, carbon dioxide, and hydrocarbons. Liquid water and hydrocarbons are removed by filtration or settling but gaseous water and hydrocarbons must be removed by other means.

The following sections of this chapter will deal with the various methods of removing these substances, and will show where such methods are applicable.

9.2 DRYING OF AIR BY SOLID ADSORBENTS

In any low-temperature process for the separation of air components, removal of water from the process air is a necessity. This removal is accomplished in some processes by freezing out the water in a heat exchanger and then deriming (see Chapter 3) as in the case of a switch exchanger, or re-evaporating as in the case of the reversing exchanger or regenerator. In addition to these mechanical methods, water removal may be effected by the use of solid adsorbents. Such a method has distinct advantages in some cases, especially where high operating pressures are employed. A particular situation where solid drying agents find application is in the removal of water from pure oxygen, which has been compressed in machines lubricated with water or an aqueous soap solution. In anticipation of a demand for data to design drying systems for the applications indicated above, an investigation of the performance characteristics of several desiccants was undertaken.

In the course of this investigation the effects of the following variables on dryer performance when using air were evaluated[1]: (1) air pressure, (2) air temperature, (3) air humidity, (4) air velocity, (5) duration of drying period, (6) desiccant used, (7) particle size of desiccant, and (8) desiccant bed length to diameter ratio. Drying performance was judged by the capacity of the bed and the exit air humidity.

Two sets of apparatus were constructed. One was for high-pressure operation and the other for low pressure. The high-pressure dryer proper was a tube with an inside diameter of 1 in. and of such length that it could be filled with from 10 to 4 in. of desiccant. Compressed air was fed to this dryer after first being passed through two water-filled saturators and a trap for entrainment removal. All units of this system were immersed in a constant-temperature bath. The discharge air from the dryer was throttled to atmospheric pressure through a dew point meter and a gas meter. No provision was made for the regeneration of the desiccant in situ.

The low-pressure dryer consisted essentially of a 42-in. section of 8-in. standard pipe set in a vertical position. Two inches from the bottom a screen, reinforced with a perforated plate, was installed to support the desiccant. Cooling coils spaced 6 in. apart were installed in the dryer, and thermocouples for the measurement of gas and bed temperatures were provided. Compressed air, to which a controlled amount of steam could be added, was fed to a suitable cooler and trap, and then to the dryer. Air from the dryer was metered by an orifice and discharged to the room. To regenerate the bed, flue gases formed by the combustion of city gas under a conical hood were drawn down through the dryer by a compressor. The compressor was protected by an ample cooler and filter, which were placed ahead of it, and the discharged gases were cooled, filtered, and metered to the room. After reactivation, the bed was cooled by passing water through the pancake coils.

In carrying out a test, saturated air at a fixed temperature and pressure was fed to the dryer, and the exit dew point was measured as a function of time. Dew points were measured with a General Electric dew-point meter and also with a homemade instrument patterned after the GE instrument.

The data obtained, and discussions of the experimental results are given in detail in the references.[4,5,6,7,9,10,11,12,13]

9.2.1 High-Pressure Air

The experiments with the high-pressure dryer covered a pressure range of 100 to 2,000 psi and a temperature range of 80 to 150 F. In all cases saturated air was used and the flow rates extended from 1,000 to 4,200 standard cubic feet of air per foot of desiccant. Drying agents of the following varieties and sizes were tested: 4- to 8-mesh alumina, 8- to 16-mesh Florite, 8- to 14-mesh silica gel, and 8- to 14-mesh potassium hydroxide. To discover the effect of bed geometry, bed length to diameter ratios of 10/1 and 4/1 were used. In preparation for the tests, the desiccants were regenerated with flue gases at 450 to 510 F for 4 hrs, except in the case of silica gel, where a regeneration temperature of 370 to 470 F was used.

The experimental results indicated bed capacities ranging from 4.9 to 13.1% and minimum dew points ranging from —30 to —109 F. It was found in general that the dew point of the exit air decreased with time to a minimum, and then remained fairly constant until the break point. This "induction period" in which the desiccant was not working at top efficiency was found in all cases except with potassium hydroxide.

In the course of the drying tests the following observations were made.

1. The break-point capacity was reduced as the temperature of drying was increased.
2. The same was true of the —70 F dew point capacity (per cent of water absorbed to bed weight when exit air humidity has reached —70 F).
3. The minimum dew point was increased (that is, the air is less dry) as the drying temperature was increased.
4. The break-point capacity was increased as pressure was increased.
5. The same was true of the —70 F dew point capacity.
6. The minimum dew point was lowered as pressure was increased.
7. Both capacities were decreased slightly as space velocity was increased.
8. Minimum dew point was unaffected by space velocity.
9. At 500 psia, space velocity of 6,000, and at all temperatures measured, the break-point capacity of silica gel was about 2½ times that of alumina. At 85 F and the above pressure and flow conditions, silica gel exhibited about four times the capacity of Florite, and at 150 F about three times.
10. The same general observations were true for the —70 F dew point capacity.
11. At the same conditions as in (9) and at all temperatures, Florite exhibited an exit dew point about 5 F above (less dry) silica gel and about 8 F above alumina. The alumina dew points varied from —100 to —78 F at bed temperature of 85 and 150 F respectively.
12. At the same pressure and flow conditions as in (9) and at 85 F, the capacity and exit dew point of potassium hydroxide was quite comparable with alumina. At 150 F, however, the exit dew point was much higher (less dry) than alumina. The capacity was not determined at this condition. Potassium hydroxide tends to channel the flow, particularly after an interruption of flow, and very poor performance results. This is probably caused by the formation of aqueous potash on the solid surfaces which can cement the particles and fill the crevices.

It was concluded that alumina was the best desiccant, particularly at high air-space velocities. Although at low velocities, silica gel was found to be superior, with respect to capacity at least, high-space velocities are desirable for practical drying applications, thus alumina is indicated. As a drying agent, potassium hydroxide was found to be unsatisfactory.

9.2.2 Low-Pressure Air

In the low-pressure apparatus the data were extended to the pressure range of 100 psi down to atmospheric. The drying agent used was 4- to 8-mesh alumina packed in a bed having a length to diameter ratio of 4/25. Flow rates used varied from 250 to 2,000 scfh per cu ft desiccant and the humidity of the inlet air ranged from 0.0005 to 0.0014 lb water per lb dry air. Regeneration of the bed was accomplished by passing flue gas at 250 to 500 F thru the bed for a period of from 1 to 5 hrs. Both adiabatic and isothermal operation were investigated.

The following observations were made in the course of the low-pressure experiments.

1. Although the effect of drying temperature was not directly measured, it was observed. Thus, adiabatic operation of the bed, which gave higher temperatures, showed considerable reduction in capacity.
2. Adiabatic operation also caused an increase in dew point of about 6 to 7 F at low-flow rates, and about 15 F at high-flow rates.
3. The capacity was increased at higher pressure operation.

4. The minimum dew point was lowered at higher pressure operation.

5. The capacity was decreased as space velocity was increased, and this effect was particularly marked for adiabatic operation.

6. The minimum dew point was relatively unaffected by space velocity in isothermal operation, but in adiabatic operation it was considerably increased at higher space velocities.

7. The capacity of the dryer was increased as the temperature of regeneration was increased. A practical maximum was 600 F where the gel begins to break down.

8. The minimum dew point was decreased as the temperature of regeneration was increased.

9. The capacity of the dryer was unaffected by the time of regeneration (between 1 and 7 hr), provided the regeneration occurred at 450 to 500 F. This was equally true of adiabatic or isothermal operation during the drying cycle.

10. The capacity of the bed was markedly reduced as the entrance air humidity was reduced, a rather unexpected and very important observation.

11. The exit dew point was markedly reduced as the entrance air humidity was reduced.

9.2.3 Design Conditions

The data obtained during this investigation of the drying of air by solid adsorbents are sufficient for the designing of dryers for most operating conditions. For high-pressure isothermal operation the following conditions may be cited as satisfactory, using alumina as a drying agent: pressure, 2,000 psi; temperature, 85 F; air saturated at above pressure and temperature; space velocity, 6,000 cu ft/hr cu ft; bed height, 4 in.; break-point capacity, 10.88%; "−70 F dew point capacity," 13.10%; and minimum dew point, −106 F.

Satisfactory conditions for low pressure adiabatic operation using alumina as drying agent may be summarized as follows: pressure, atmospheric; inlet temperature, 70 to 80 F; bed height, 34 in.; space velocity, 980 cu ft/hr cu ft; break-point capacity, 2.56%; minimum dew point, −86 F.

For isothermal operation under the latter conditions the capacity would be 5.5% and the minimum dew point −90 F.

For the development of the component parts of several oxygen plants the drying data obtained in the investigation outlined above proved useful in the design of dryers used in purifying air for process use both at high and low pressures.[11]

9.3 REMOVAL OF CARBON DIOXIDE FROM AIR BY CAUSTIC SOLUTIONS

A simple method for removal of carbon dioxide from air consists of scrubbing the gas with a caustic solution in an apparatus which affords intimate contact between the two phases. Such a scheme has been widely used for gases containing relatively high concentrations of carbon dioxide, and data were available for the design of such systems. For carbon dioxide concentrations as low as that found in atmospheric air (330 ppm), however, data for use in design were signally lacking. Since adequate purification procedures were essential to some oxygen processes and most useful in the preliminary development of the individual components embodied in any plant, an investigation was undertaken to evaluate the performance of a packed column in the removal of carbon dioxide from atmospheric air by means of a caustic solution.[14,15] As an extension to this program, the possibilities of another type of apparatus, the jet-type absorber, were given consideration, and preliminary data obtained.

The investigation of packed towers was undertaken to obtain data for use in the design of commercial size units and two 12-in. diameter towers were built as experimental units. One of these towers was designed for use in studies involving operation on the suction side of a compressor while the other was designed for use at higher pressures (up to 300 psia) on the discharge side of a compressor. The effect of the following variables was studied: air rate, liquor rate, operating pressure, packed height, and the comparative scrubbing efficiences of aqueous sodium and potassium hydroxide solutions. The effect of alkali concentration and the degree of conversion to carbonate was fairly well known from previous work with CO_2-rich gas mixtures so that very little time was devoted to a study of these factors.[1]

The packed tower used in experiments at atmospheric pressure was designed on the basis of available data from the literature on the absorption of CO_2-rich gas mixtures by alkalies.[2] The diameter was 12 in. and the height 18 ft; 3/4-in. stoneware Raschig rings were used as packing. The construction of the tower allowed a maximum packed height of 16 ft, although in some cases less packing was used. This tower is shown in Figure 1. The flow sheet for the low-pressure system is shown in Figure 2.

From the data obtained at atmospheric pressure on the above tower, another tower was built to permit extension of the studies to elevated pressures. This tower was made 16 ft high to allow for liquor storage within the tower body and yet give a packed height of 10 ft (Figure 3). The packing used in this tower was 1-in. Berl saddles. The flow sheet for the high-pressure system is shown in Figure 4.

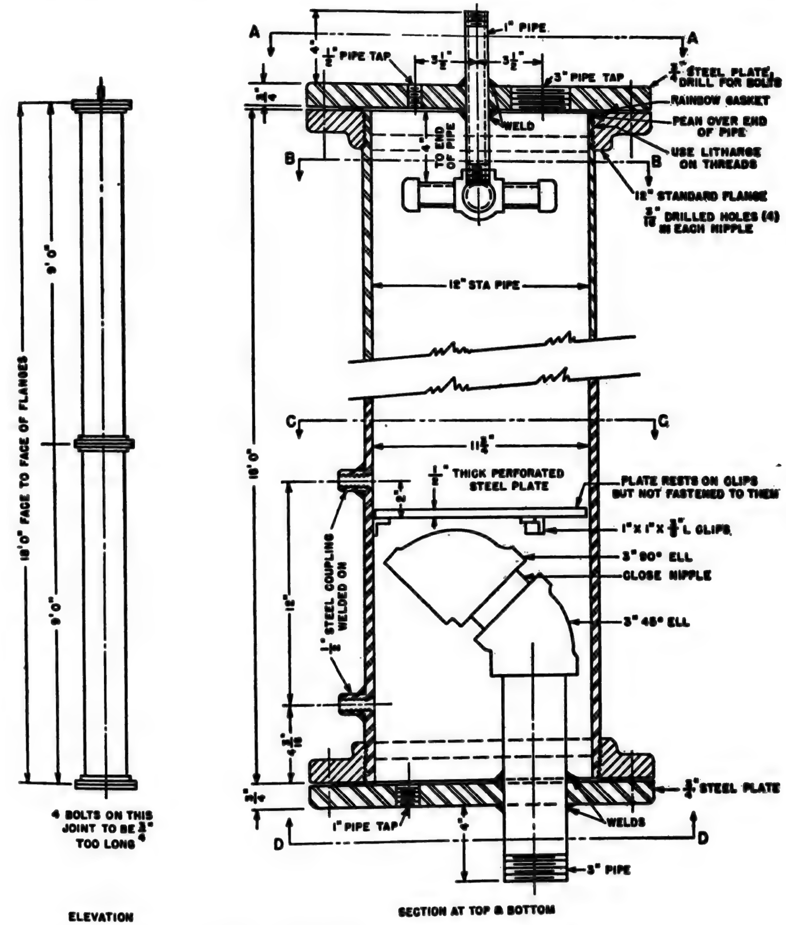


FIGURE 1. Low-pressure carbon dioxide scrubbing tower.

In all the experimental runs, atmospheric air was used and the CO_2 concentration did not vary appreciably from the value of 0.0315% usually found in clean air. For the most part, a 2.5N aqueous sodium hydroxide solution was used, previous work having indicated this to be the optimum alkali concentration. Previous investigators had also determined the effect of the degree of conversion of the alkali to the carbonate, and the solutions were always changed before this conversion became great enough to have an effect on the absorption coefficient. All the runs were made at the prevailing room temperatures.

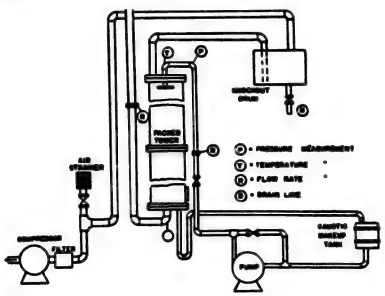


FIGURE 2. Flow sheet for low-pressure scrubber.

In the course of the experiments, the effect of liquor rate on the absorption rate coefficient was determined at several conditions of packed height and gas rate. The results of these tests are shown graphically in Figures 5, 6, and 7. It was found that K_ga, the overall absorption coefficient, based on the gas phase, varies as the 0.20 power of the liquor rate. Absolute values of the coefficient for various conditions can be obtained from the plots.

From the data included in Figures 5, 6, and 7 the relationship between K_ga, the overall coefficient, and G, the gas rate, was found to be of the form, $K_ga = 0.35 \log G + C$ for values of G up to 500 lb per hr per sq ft. Above this value the effect of gas rate becomes less marked, and for gas rate values of about 1,000 lb per (hr) (sq ft), K_ga varies only as the 0.15 power of the gas rate. The relationship between the overall absorption coefficient and the gas rate is illustrated in Figure 8.

In the packed tower tests, three different packed heights were used. Performance of the tower as related to packed height was somewhat erratic as shown in Figure 9. A partial explanation for the observed effects of packed height can be made by considering the conditions under which the data were obtained. For the shortest packing height the liquor distribution may have been better and there might also have been some wetted wall effects in the empty tower section above the packing. In the case of the 10-ft packed height, the coefficients were lower than for the 16-ft height. Tests for the 10-ft height were made in the high-pressure tower where this was the maximum packing height and end effects were eliminated. Also, for the high-pressure tower, the air processed was quite oily, and fouling of the packing may have occurred. Another factor to be considered in explaining the apparent discrepancies in the results of the packing height studies is the fact that for the 10-ft height 1-in. Berl saddles were used whereas Raschig rings were employed in the case of the other packing heights.

Some tests were made to compare KOH and NaOH solutions for scrubbing efficiency.[3] The results obtained are illustrated in Figure 10. Analysis shows that the values of the overall absorption coefficient obtained, using a KOH solution, are from 20 to 30% greater than those for a NaOH solution of equal normality. This difference is probably due in part to the different physical properties of KOH solution. For KOH solutions, K_ga varies only as the 0.10 power of the liquor rate. If higher transfer coefficients were to be explained by increased reaction rate between KOH and CO_2, the relative importance of the liquor rate would necessarily increase. Since this is not true, the superiority of KOH solution over NaOH solution as a scrubbing agent is most probably due to differences in physical properties as noted above.

The effects of operating pressure on packed tower performance in the removal of CO_2 from atmospheric air were studied in the high-pressure tower previously described. The results, shown graphically in Figures 11 and 12, indicate that K_ga decreases as the 0.5 power of the absolute pressure of tower operation. This effect was independent of gas and liquor rates. At the higher pressures, the variation of K_ga with liquor rate becomes less and the effect of gas rate increases.

In addition to the packed tower tests, the potentialities of a jet-type absorber were studied. The jet-type scrubbers investigated consisted, basically, of variable length-absorption tubes in series with in-

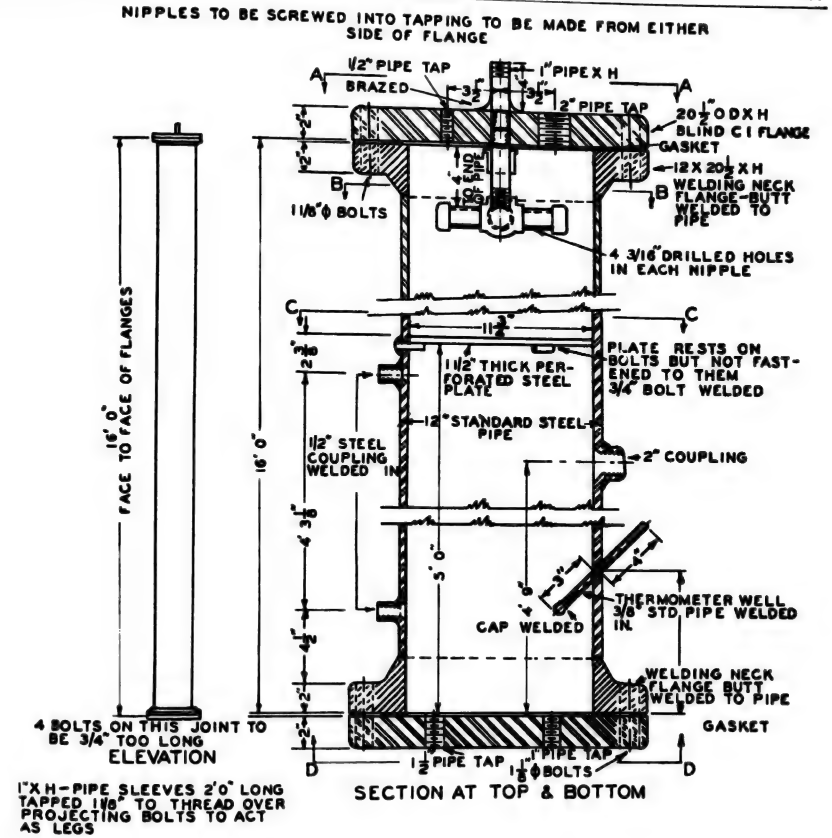


FIGURE 3. High-pressure carbon dioxide scrubber.

jectors. Actual mixing of the air and caustic was accomplished in the injector, and the mixture discharged into a horizontal tube, where absorption continued until the gas and liquid streams were finally separated. The operating characteristics of the jet-type scrubber were determined, and the effect of liquor rate, gas rate, length of absorption tube, diameter of absorption tube and injector type on absorption performance was studied.[14]

From the data obtained, it was evident that the liquid rate had very little effect on the absorption coefficient. Over the flow ranges investigated, the gas rate was found to have an appreciable effect on the absorption coefficient as shown in Figure 13. K_ga appears to be a linear function of the gas rate ($K_ga = 9.1 + 23.5\,V$, where V is the volume of the absorber in cubic feet).

The information obtained in the investigation of packed tower performance outlined above makes possible the design of scrubbing systems for the re-

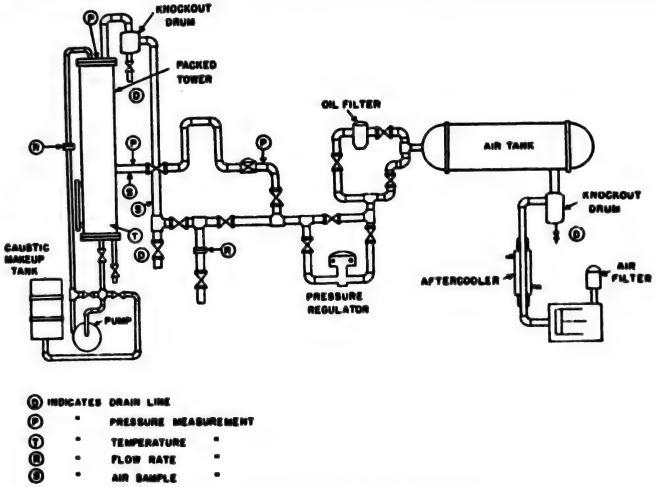


FIGURE 4. Flow sheet for high-pressure scrubber.

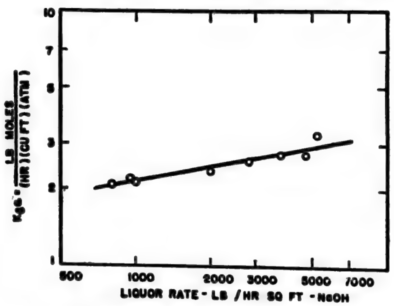


FIGURE 5. Absorption of carbon dioxide by sodium hydroxide in a packed height of 16 ft.

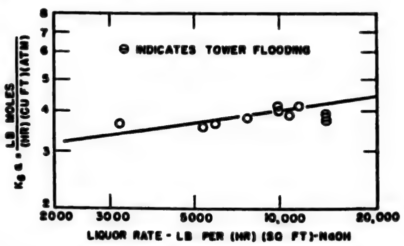


FIGURE 6. Absorption of carbon dioxide by sodium hydroxide in a packed height of 7.8 ft.

moval of carbon dioxide from atmospheric air. Such a system was actually built for use in the testing and development of oxygen plants and their component parts.[16,24] The work done with the jet-type scrubber indicated the potentialities of such a device, especially where size considerations are important.[24] The limited amount of work done with the jet-type scrubber prevents any conclusions as to optimum conditions and dimensions, but from the data now available an absorber of this type can be designed for a given job.

9.4 REMOVAL OF CARBON DIOXIDE FROM HIGH-PRESSURE AIR BY MEANS OF SOLID ABSORBENTS

The removal of carbon dioxide from the air feed to air liquefaction-rectification units can be accomplished in numerous ways, such as by condensation to a solid at low temperature and removal by deposition or filtration, by washing the air with a solution of caustic alkali, by passing the air over a bed of a solid absorbent such as potassium hydroxide or soda lime, or by adsorption on an active adsorbent such as carbon or alumina.

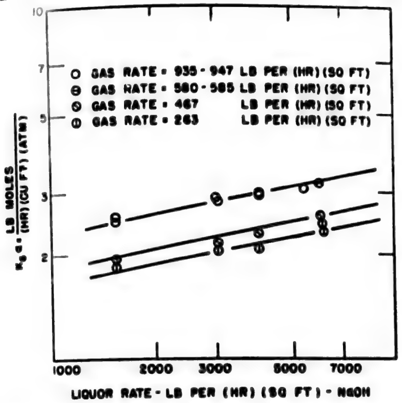


FIGURE 7. Absorption of carbon dioxide by sodium hydroxide in a packed height of 10 ft.

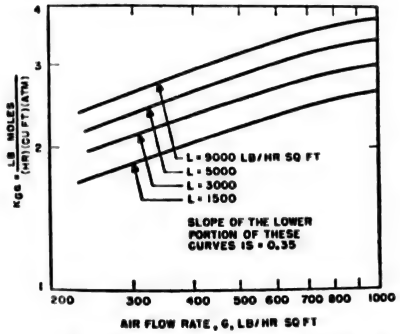


FIGURE 8. Relation between absorption coefficient and gas flow.

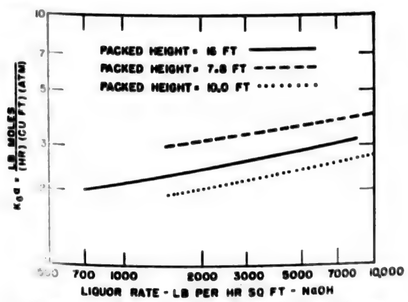


FIGURE 9. Effect of packed height on absorption coefficient.

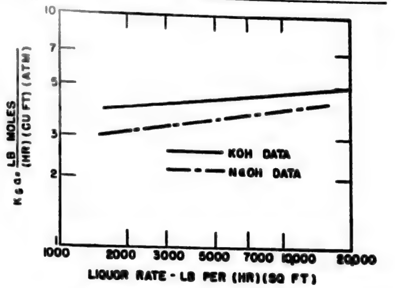


FIGURE 10. Absorption of carbon dioxide by sodium-hydroxide and potassium-hydroxide solutions.

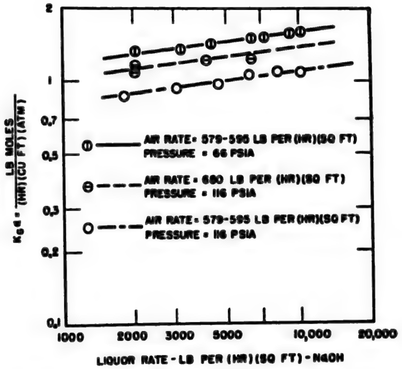


FIGURE 11. Carbon dioxide absorption at elevated pressures.

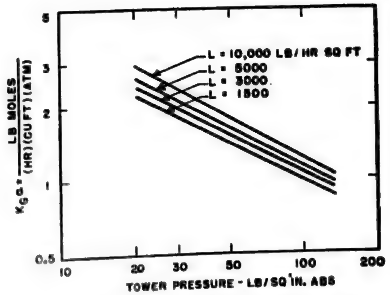


FIGURE 12. Effect of liquor rate on absorption coefficient at elevated pressures.

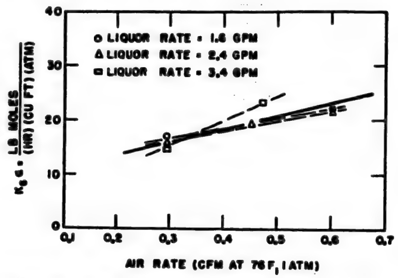


FIGURE 13. Effect of gas rate on absorption coefficient.

All these methods are employed in the various oxygen-producing units in use by the Armed Services or developed under the NDRC. Certain of them have been the subject of fundamental study. This section deals with the results of a study of the removal of carbon dioxide from high-pressure air by means of solid alkaline absorbents at ordinary temperatures and by active absorbents at low temperature.

A fundamental study of CO_2 absorbents embracing the widest possible range of temperatures, pressures, and CO_2 concentrations was beyond the limitations of time available. Since solid absorbents are used only in the high-pressure units in which Section 11.1 was interested, attention was centered upon operation at 3,000 psi; and since soda lime seemed preferable to caustic alkalies in most high-pressure units which now use chemical clean-up, attention was centered largely upon soda lime in this work.

Existing information concerning the use of solid absorbents for CO_2-air mixtures such as are represented by a normal atmospheric air (CO_2 at 300 to 400 ppm) was very meager. A rather restricted study of the use of soda lime for CO_2 removal from high-pressure air has been carried out by E. B. Badger and Sons Company but this work is of limited scope. Their results afford little basis for the design of absorption equipment for units operating under other conditions of flow rate and CO_2 tolerance than those obtaining in the Air Reduction Company unit with which the work was done. The criteria of absorbent performance were simply the appearance of the liquid oxygen draw-off (milky or clear) and the plugging of the unit. No CO_2 analyses were carried out.

In the present work, the performance of the absorbent was followed by continual analysis of the air under treatment and, to some extent, by analysis of the exhausted absorbent. Some attention was paid to the water relationships with the object of determining whether or not the absorbent possessed drying properties. The data have been evaluated in such a way as to allow reasonable extrapolations to be made.

It was not possible in the time spent to study the effect of temperature and pressure variation (except for some data at about atmospheric pressure), but certain conclusions have been possible concerning the effect of variations in the concentration of CO_2 in the air. The chief variables studied were the effect of flow rate, linear velocity and, in the case of soda lime, mesh size.

9.4.1 Carbon Dioxide Analytical Methods

The requirements of an analytical method suitable for the purposes of this work follow.

1. Accuracy and reliability for CO_2 concentrations of about 5 to 500 ppm (0.0005 to 0.05%).
2. Rapidity, so that a continuously changing exit concentration can be followed.
3. Freedom from the need for observing elaborate precautions to prevent contamination by ordinary laboratory air, or by CO_2 containing confining solutions (it must not be necessary, for example, to store samples over water or other liquids before analysis).

These requirements immediately rule out such obvious methods as absorption by ascarite and weighing, titration of a large sample of air by standard alkali (the classical Pettenkofer method), the Van Slyke manometric method and the standard gas analysis techniques including that using the sensitive Haldane apparatus. A specific example of the numerical magnitude of the quantities in a single analysis is: a 1-liter sample of air containing 50 ppm of CO_2 contains 0.05 ml or 0.1 mg of CO_2, equivalent to 0.45 ml of 0.01*N* alkali. It is apparent that the measurement of small quantities such as these could not be done both accurately and rapidly, and that minute amounts of contaminants would introduce large errors. It is necessary, then, to increase the sensitivity of the method, or to find a way to collect and analyze a very large sample in such a way as not to introduce contaminants either during the sampling or during the determination of the CO_2.

Two very sensitive "relative" methods of CO_2 determination have been used, both of which require calibration and repeated standarization with mixtures of known CO_2 content.

The Colorimetric Method

This method, developed early in the program[a], depends upon the destruction by CO_2 of the color of a solution of the sodium salt of phenolphthalein. The method can be made very sensitive by a suitable choice of the concentrations of alkali and phenolphthalein, and of the ratio of gas sample volume to reagent volume. The procedure consists in agitation of a sample of the air to be analyzed with a definite volume of the indicator solution, followed by a colorimetric measurement of the change in transmission so produced. The slope of the calibration curve, which is a plot of *log transmission* vs CO_2 *content of the sample*, is established by two points, one being the transmission of the original solution which has been carried through the manipulative procedure with a CO_2-free gas, the other being the point obtained with a sample of gas of accurately known CO_2 content.

Extensive use of this method has shown that it must be checked frequently, that it is often subject to unexplainable aberrations, and that it is capable of satisfactory precision only if considerable care is taken both in sampling and in carrying out the analysis. The data of Figure 19 were obtained by this method, and the scattering of the points is an indication of the kind of results it is capable of when a series of samples of continuously changing CO_2 content are taken.[24]

The Pfund Gas Analyzer

Developed under Division 17, NDRC, the Pfund meter has proved to be completely satisfactory for the continuous analysis of exit gas samples. The instrument is very sensitive, gives rapid readings and, except for some uncertainty at low (15 ppm) concentrations of CO_2, is capable of considerable accuracy.[19,20,21] This instrument utilizes the infrared absorption of CO_2; it has been described in Division 17 reports. The setup in which the instrument was used is shown in Figure 14. The ascarite scrubber is used to supply the analyzer with a CO_2-free sample for zero adjustment; when a reading is taken, the ascarite is bypassed (valve *A* closed, *B* open).

Most of the analytical data reported were obtained with the Pfund gas analyzer.

"Absolute" Methods

Both the colorimetric method and the Pfund analyzer are relative, and must be calibrated with a sample of known CO_2 content. Experience has shown that it is not safe to rely either upon the constancy of atmospheric air or upon known samples prepared by mixing CO_2 and CO_2-free air in storage tanks for the required standard mixture. It was deemed preferable to devise a method, however elaborate, by which a standard source (for example, a tank of air) could be analyzed with accuracy, and to use this standard mixture for calibration of the relative methods.

A number of experiments were carried out to examine the possibilities of absorption on ascarite and weighing, and absorption in standard alkali, followed by back-titration. It was concluded that, with care and the observance of numerous precautions, ascarite can be used for samples of air containing 200 to 400 ppm, but the errors introduced by traces of moisture and by the uncertainties of weighing ascarite bulbs weighing 50 to 100 g, could cause large inaccuracies.[24] The titration method, in which air was continuously passed through standard alkali and the excess alkali back-titrated, was very unsatisfactory.

The method finally devised and adopted is a titration method which avoids the errors introduced by exposure of the alkali to laboratory air, and by means of which a large sample can conveniently be taken, without necessitating the use of large and unwieldy sample containers. It consists of a sample bottle containing the standard alkali into which repeated samples of the air to be tested can be drawn, each sample being removed by evacuation after absorption of the CO_2. The essential feature of the method is the titration without removing the sample of essential alkali from the reaction vessel.[24]

In connection with some studies started after the CO_2 absorption study was completed, this "absolute" method was modified to make the procedure simpler and to make the method applicable to very low CO_2 concentrations. This modification consists in passing the air sample to be studied through a copper coil immersed in liquid air, at which temperature substantially all of the CO_2 is condensed to a solid.[28]

The condensed CO_2 is allowed to expand, and is finally flushed into the titration vessel and titrated as in the method above. The volume of air sample that can be taken in this way is practically unlimited, the rate at which it can be taken being limited only by the heat transfer characteristics of the condensation coil.

As a numerical illustration of the quantities that are dealt with in this method, consider a sample of 20 liters (20/28.3 ft³) of air containing 300 ppm

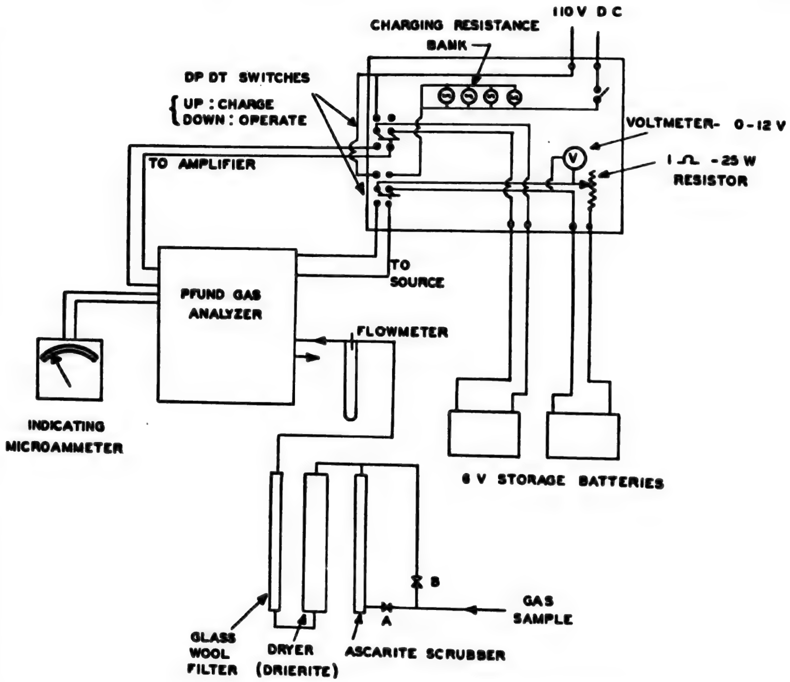


FIGURE 14. Electrical and sampling setup for use with Pfund gas analyzer.

CO_2. This would consume about 27 cc of 0.02*N* alkali. A 200-l sample of air containing 30 ppm would consume the same amount of alkali. It is apparent that considerable precision is possible.

9.4.2 Apparatus and Equipment for Absorption

AIR SUPPLY

For runs at pressures above atmospheric, the air was supplied by a Norwalk compressor capable of delivering about 100 scfm at 3,000 psi. The intake to this compressor was located in a duct which took air from a point about 70 ft above the ground.

BOMBS

Early runs were made using a bomb which held about 7 lb of 4- to 8-mesh soda lime, and was charged in layers which could be separately removed and examined. It was soon found that the use of so large a charge was impracticable because the amount of air required could not be obtained when other units required air from the Norwalk compressor. Most of the work was carried out using the small bomb shown in Figure 15. This bomb held about 1 lb of soda lime, and runs could be made at linear velocities comparable to those expected in practice without using excessively large amounts of air. The small bomb was much more convenient to recharge and install.

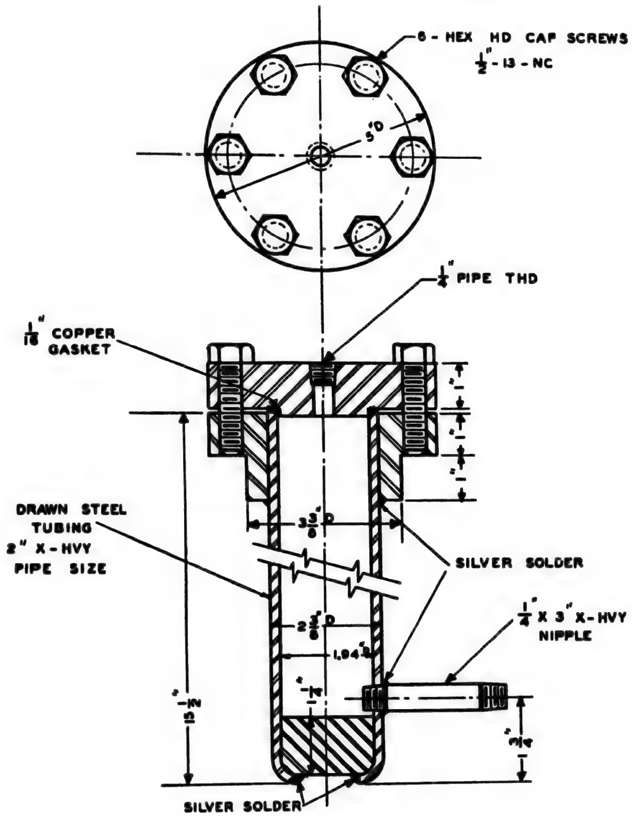


FIGURE 15. High-pressure bomb.

THE PIPING ARRANGEMENT

The piping arrangement used for all the runs with the small bomb is shown in Figure 16. Essentially the same setup was used for the runs with the large bomb.

The cooler in the inlet air line was generally maintained about 3 to 4 C below room temperature so that the air entering the absorbent was slightly under saturation. This was done to prevent the possibility of actual condensation of water in the absorbent bed.

APPARATUS FOR LOW-TEMPERATURE ADSORPTION

Experiments were made in a jacketed bomb in which the adsorbent was placed and through which the precooled test air was allowed to flow. The arrangement is shown in detail in the diagram of Figure 17. The exit and inlet air were analyzed by the Pfund analyzer.

For reasons which will be given in a later section, a series of experiments were carried out at a temperature of -78.5 C (dry-ice) and at atmospheric pressure.

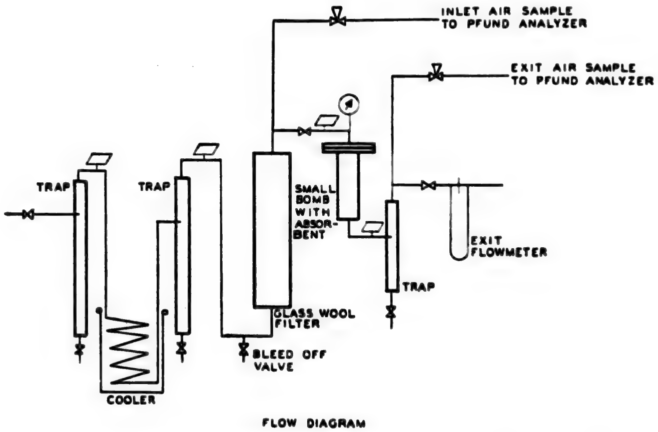


FIGURE 16. Flow diagram for high-pressure absorption.

MATERIALS

Soda Lime. The soda lime used was purchased from the Dewey and Almy Chemical Company, Boston, Massachusetts. It was obtained in two mesh sizes: 4 to 8 and 14 to 20; and in high-moisture (16%), and low-moisture (less than 2%) grades.

Soda lime is substantially a mixture of calcium, sodium, and potassium hydroxides; the material used in this work (Wilson soda lime) contains about 5% caustic alkalies, the remainder being calcium hydroxide and a small amount of inerts (including some calcium carbonate).

Potassium Hydroxide. The pellet grade, as commonly used in chemical laboratories, and Niagara Alkali Works flake grade, were used.

Sodium Hydroxide. Two forms of this were used: pellets, and a flake form furnished by the Wyandotte Chemical Company.

Baralyme. Baralyme is a proprietary name used for a mixture of barium and calcium hydroxides [about 20% $Ba(OH)_2$] manufactured by Thomas A. Edison, Inc., East Orange, N. J.

Active Carbon. A number of active (gas purification) charcoals were obtained from commercial sources. These are identified in the section in which their testing is described.

Others. A variety of active adsorbents other than active carbons were tested. These are described in the section in which their testing is described (see Table 1).

9.4.3 **Experimental Procedure**

ALKALINE ABSORBENTS

A few early runs were made using the large bomb, which was installed at the same point as the small bomb shown in Figure 16. The soda lime was charged in eight layers of 0.845 lb each, separated by disks of copper gauze. In these runs the colorimetric method of CO_2 analysis was used. During the runs the inlet and exit air streams were analyzed at intervals for CO_2 and at the completion of a run the various layers of soda lime were removed separately, sampled and analyzed for moisture and CO_2 content.

For reasons mentioned in an earlier section the large bomb was later discarded and all succeeding runs were made using the small bomb. In most of these runs no analyses of the exhausted charge were made. The inlet air stream was analyzed at intervals and, unless marked variations were observed, was assumed to remain substantially constant; observations extending over many months have shown that the CO_2 content of the air taken into the roof-

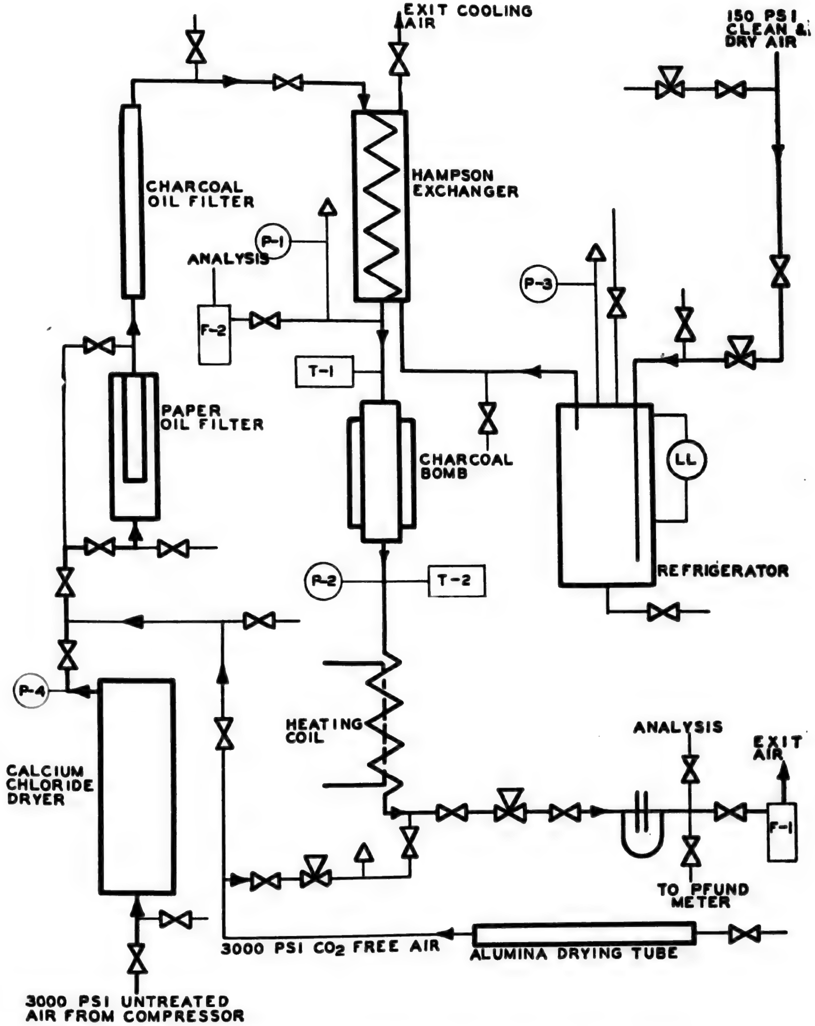


FIGURE 17. Flow diagram and high-pressure sorption of carbon dioxide on charcoal.

level duct seldom varied outside the limits 320 to 350 ppm. Exit air analyses were made sufficiently often to define clearly the slope and shape of the breakthrough curve.

The flow rate was measured after expanding the air to atmospheric pressure. Readings were taken of the pressure and temperature points shown on the flow sheet (Figure 17).

were made, no breakthrough curves were needed, and analyses of the exit and inlet air streams were made only for the purpose of recognizing when the adsorbent was saturated (that is, exit CO_2 concentration—inlet CO_2 concentration). When this point was reached, the adsorbent was allowed to warm up, and the desorbed CO_2 was collected on ascarite and weighed.

Table 1. Adsorption of CO_2 from ordinary air at −78 C, atmospheric pressure.*

Material	Treatment	Number of runs	Adsorption† grams CO_2 per g
Silica gel	Pumped out at 200 C, 2 hr‡	3	0.0117
Silica gel impregnated with Cr_2O_3§	Heated at 300 C, 8 hr	4	0.0105
CWSN 249 AY carbon	As received	2	0.0081
Silica gel	As received	1	0.0080
Silica gel impregnated with Cr_2O_3§	Pumped out at 200 C, 2 hr‡	1	0.0069
Activated alumina	Pumped out at 200 C, 2 hr‡	2	0.0067
Columbia 4ACW carbon	As received	3	0.0065
Columbia 6G carbon	As received	2	0.0063
CWSN 291 AY carbon	As received	1	0.0063
Activated alumina	Heated at 180 C, 3 hr	3	0.0061
CWSN 17-6 carbon	As received	1	0.0060
Silica gel impregnated with Cr_2O_3§	Heated at 280 C, 4 hr	1	0.0057
Pittsburgh C. and I. Company carbon	Pumped out at 200 C, 2 hr‡	3	0.0054
Pittsburgh C. and I. Company carbon	As received	2	0.0050
Cr_2O_3 (gel)	Heated at 280 C, 4 hr	1	0.0032
Cr_2O_3 (precipitated)	Dried at 150 C	1	0.0024
Cr_2O_3 (gel)	Heated at 300 C, 2 hr	2	0.0008
Fe_2O_3 (precipitated)	Heated at 300 C, hr	2	0.0003

* Inlet air contained about 320 to 340 ppm CO_2.
† Saturation value. Runs continued at least 1 hr after analyses showed CO_2 concentration in exit air = CO_2 concentration in inlet air.
‡ Samples pumped out at full vacuum of Hy-vac pump.
§ Contained about 9% by weight of Cr_2O_3.

Adsorption at Low Temperature

At 3,000 psi. The precooled air stream was passed through the adsorbent, the temperature of which was maintained entirely by the air passing through it and measured by inlet and outlet thermocouples. The air was expanded through a reducing valve and the flow measured at atmospheric pressure. The CO_2 content of the inlet and exit air streams was measured frequently by means of the Pfund analyzer. At the completion of a run (that is, when complete breakthrough was observed) the adsorbent was allowed to warm up slowly, the desorbed CO_2 being absorbed in tared ascarite bulbs and weighed.

At Atmospheric Pressure. For the purpose of obtaining a rapid comparison of a number of adsorbents, the experimental difficulties involved in regulating and maintaining accurate temperature control in the high-pressure unit were avoided by carrying out a series of runs using air at ordinary pressure, and cooling the adsorbent in a bath of acetone-dry ice (Figure 18). For the purposes for which these runs

In all cases, duplicate runs were carried out whenever there was any question as to the validity of the results or when, for any reason, considerable changes in operating conditions (flow, temperature, pressure, etc.) occurred during a run. In some series of experiments all runs were made in duplicate.

9.4.4 Experimental Results

Alkaline Absorbents

Low-Moisture Soda Lime. A series of nine runs (TC 13–22) were made with 4- to 8-mesh, low-moisture (2%) soda lime. A charge of 1 lb was used in the small bomb (about 13-in. bed depth) and flow rates of 400 to 1,600 scfh (at 3,000 psi) were chosen.

These runs were started with the original intention of determining the effect of flow rate upon the initial slope of the breakthrough curve, and were later extended for longer durations when the surprising observation was made that, after a certain period of operation, the efficiency of the partially exhausted

absorbent increased (that is, amount of breakthrough decreased). The experimental data and a plot of the percentage of CO_2 not removed are given in Figure 19. This quantity is used in most of the plots which present the original data and is the ratio [(ppm CO_2 in exit air / ppm CO_2 in inlet air) × 100] vs total air, scf per lb of soda lime.

analyses in these runs were carried out by the use of the colorimetric method it cannot be said with certainty that the differences in the initial portions of the curves of Figure 19 are significant. It is quite possible that, over the range of flow rates studied, all of the data up to total air flows of 500 scf per lb fall on a single line.) The important conclusion to be

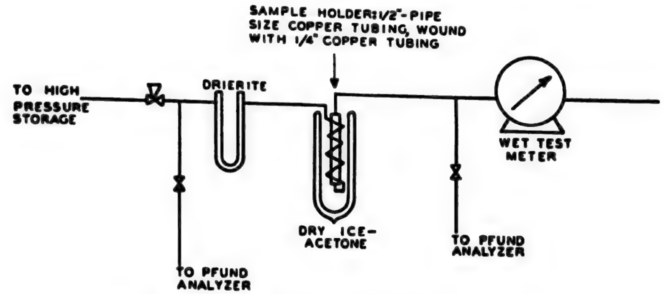


Figure 18. Flow diagram for atmospheric pressure absorption runs.

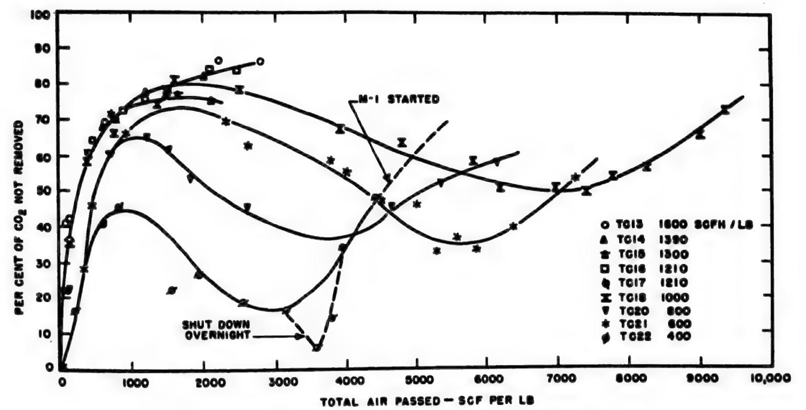


Figure 19. Breakthrough curves for low-moisture soda lime.

It is seen that for flow rates of 1,000 scfh per lb and over, all the points fall on one curve. For lower flow rates, down to 400 scfh per lb, the curves have about the same initial slopes as at higher flow rates, but reach their maximum sooner. (Since the CO_2

drawn from these data is that even at relatively low flow rates (400 scfh per lb of soda lime, or 135 scfh per sq in. bed area) low-moisture soda lime permits rapid and extensive breakthrough, and at no time in its life does it remove all of the CO_2 from the air.

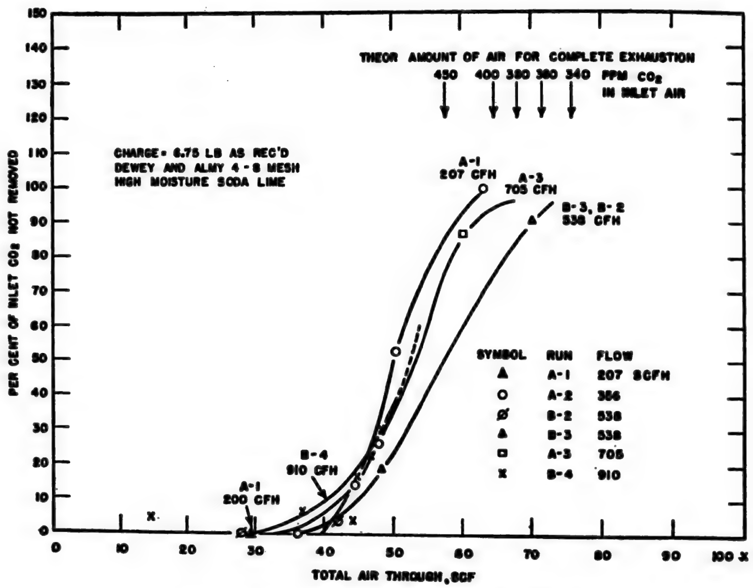


FIGURE 20. Breakthrough curves for high-moisture soda lime.

It is of interest to note that the point at which the minimum in any curve of Figure 19 is reached depends upon the total height of the curve (or upon the position of the maximum).

A reasonable explanation both for this observation and for the general shape of these curves has been adduced from a consideration of the mechanism of the soda lime-CO_2 reaction.

High-Moisture Soda Lime. Runs made using high-moisture soda lime fall into several distinct groups. The first seven runs were made using 4- to 8-mesh material in the large bomb. Succeeding runs were made using the small bomb, and fall into several groups. The results of these runs are largely inconclusive, and are presented in Figure 20. It was in an attempt to extend these runs that the low-moisture soda lime runs were made.

Of greater interest are two other sets of data taken in these experiments. These are derived from chemical analyses of the various layers removed from the bomb, and afford some information regarding the progress through a bed of the zone of exhausted absorbent and the water relationships involved in the use of high-moisture soda lime.

In Figure 21 are shown the results obtained by analyzing the separate layers for CO_2 content. It is observed that at the lowest flow rate used (Run A-1;

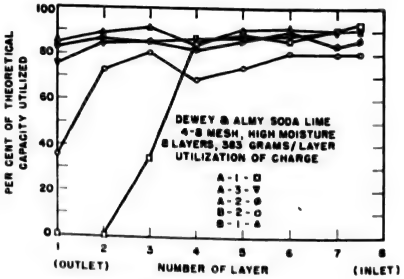


FIGURE 21. Capacity of high moisture soda lime.

30 scfh per lb) a sharp "front" exists in the bed. In run B-2, which was discontinued when 96% of the inlet CO_2 was still being absorbed, the outlet layer is beginning to be used up while none of the other layers is yet completely exhausted. Runs A-2, A-3, and B-1 were unfortunately continued too long and the results are inconclusive.

It is evident that only at very low rates of flow does a sharp concentration front exist in a soda lime bed, and it is also apparent that even extensively exhausted material can still function at high efficiency providing a low flow rate is used.

Water Relationships

A great deal of water is liberated in the reaction between soda lime and CO_2. The overall reaction may be written

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O. \quad (1)$$

For every 100 g of soda lime, 16.8 g of water is produced, for 90% exhaustion. The fate of this water is of practical importance in the use of soda lime. The water formed cannot be carried off in the exit air because the inlet air is saturated, or nearly so. It will thus remain in the bed, or in the bomb, or be carried over by entrainment.

It is apparent that in the use of soda lime for the cleanup of high-pressure air, the system must be so designed that the large amount of water evolved in the reaction cannot escape into the exit lines leading to other parts of the unit. Suitable traps or dead spaces in the soda lime vessels must be provided.

It should also be emphasized that drying systems devised for use in a system in which soda lime is used must be designed to handle air which is saturated with water. It has been shown in the preceding paragraph that to attempt to shift part of the drying load to the soda lime by the use of the low-moisture grade will result in imperfect CO_2 removal.

Small Bomb Total Cleanup Runs

The log-log plot has proved the most suitable method of plotting data such as these, since experience has shown that the initial rise in exit concentration follows a straight line, thus allowing aberrations and inconsistencies in the data to be recognized.

In order to use the log-log plot, however, one arbitrary assumption had to be made for convenience in plotting; this is that the breakthrough point (CO_2 just appearing in the exit stream) is equivalent to "1% not removed" (99% cleanup). Since this value represents an actual exit CO_2 concentration of 3 to 4 ppm it is about the smallest amount that the methods of analysis can detect with certainty. (See Figure 22.) As an example of the usefulness of this way of presenting the data, consider operation at 600 scfh per lb; CO_2 will begin to appear in the exit stream after 5.1 hr of operation. At 200 scfh per lb cleanup will be complete for 29 hr. Thus, assuming a fixed flow rate, the use of three times as much soda lime will permit six times the operating life.

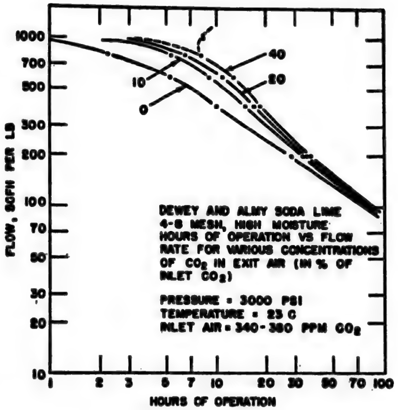


FIGURE 22. Capacity of high-moisture soda lime.

The advantage of operating at low flow rates decreases as the tolerance for CO_2 in the exit stream increases. For example, if operation can be continued until 10% of the inlet CO_2 is appearing in the exit stream, 600 scfh per lb will allow operation for 9 hr, while 200 scfh per lb will allow operation for 33 hr. In Figure 23 are shown curves which represent comparisons of this sort over a range of CO_2 tolerance and flow rates. The results are plotted as *relative efficiencies,* comparisons being made to 200 scfh per lb. For example, to operate to initial breakthrough with a flow of 800 scfh per lb a run of 2.2 hr can be made; at 200 scfh per lb a run of 29 hr, an advantage of 13.2 in relative times. If 800 scfh per lb were as *efficient* as 200 scfh per lb the lower flow

rate would permit operation for only four times as long a period. Thus,

Relative efficiency of 200 scfh per lb over 800 scfh

$$\text{per lb} = \frac{13.2}{4} \times 100 = 340\%. \qquad (2)$$

From Figure 23 it can be seen that the smaller the ratio of high flow to low flow the lower is the relative efficiency, and the greater is the amount of CO_2 that can be tolerated in the excess air.

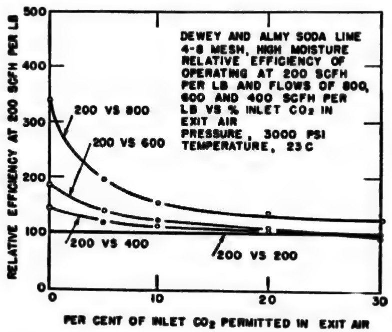


Figure 23. Relative efficiency of high-moisture soda lime at various flows.

Effect of Mesh Size

14- to 20-mesh soda lime is markedly more effective than 4- to 8-mesh material particularly at higher flow rates. The difference between them would be expected to be smaller the lower the flow rate, since in the limit, at an infinitely low rate, they would be equal in effectiveness.

Since, as will be shown later, low linear velocities should be used for maximum efficiency in the utilization of soda lime, and the pressure drop through a bed operating at 3,000 psi is inconsiderable, it is clear that 14- to 20-mesh soda lime is definitely to be preferred to 4- to 8-mesh material. The holdup and entrainment of water would be expected to be greater in the bed of smaller mesh material, and this fact should be recognized in the design of the cleanup system.

Direction of Flow through the Absorbent

Runs were performed with the direction of flow downward through the bed; these runs are compared in Table 2, with the runs described in the preceding section in which the flow was upward through the bed.

Table 2

Direction of flow	Flow, scfh per lb	Total flow, scf per lb, to 3% breakthrough	Total flow, scf per lb, to 10% breakthrough
Bottom to top	800	4,750	5,200
Top to bottom	800	4,200	5,900
Bottom to top	1,200	4,500	5,400
Top to bottom	1,200	3,800	4,800

All runs on 14- to 20-mesh, high-moisture soda lime

It is seen that there is a small but definite advantage in operating with the flow upward through the bed. This is probably due to the fact that water draining from the soda lime is held in the bed, whereas in downward flow it is continuously removed. It is to be remembered that this water is in reality a solution of alkali hydroxides which are leached from the soda lime particles. Removal of this water leaves alkali-deficient soda lime; and its scrubbing action when held in the bed certainly contributes to the CO_2 removal from the air being treated.

It can be concluded further from these considerations that a properly designed cleanup system would include some provision for the air to be scrubbed by the liquid draining from the bed before it entered the soda lime itself. Perhaps a suitable arrangement would be one in which a short section packed with some inert contact material (for example, Berl saddles) would be provided below the soda lime section, forming a short scrubbing tower in which the draining liquid could collect.

Linear Velocity Studies

A limited amount of work was done in an attempt to determine the effect of linear velocity on the efficiency of 4- to 8-mesh soda lime at constant space velocity. The results are not entirely concordant and are too scanty to permit significant conclusions being drawn. The breakthrough curves are plotted in Figure 24.

It appears that a certain value of linear velocity (0.03 to 0.05 ft per sec) must be reached before maximum effectiveness is obtained, and that a further increase offers no advantage. The data are too meager to allow much more to be said, and circumstances prevented an extension of this line of attack at the time.

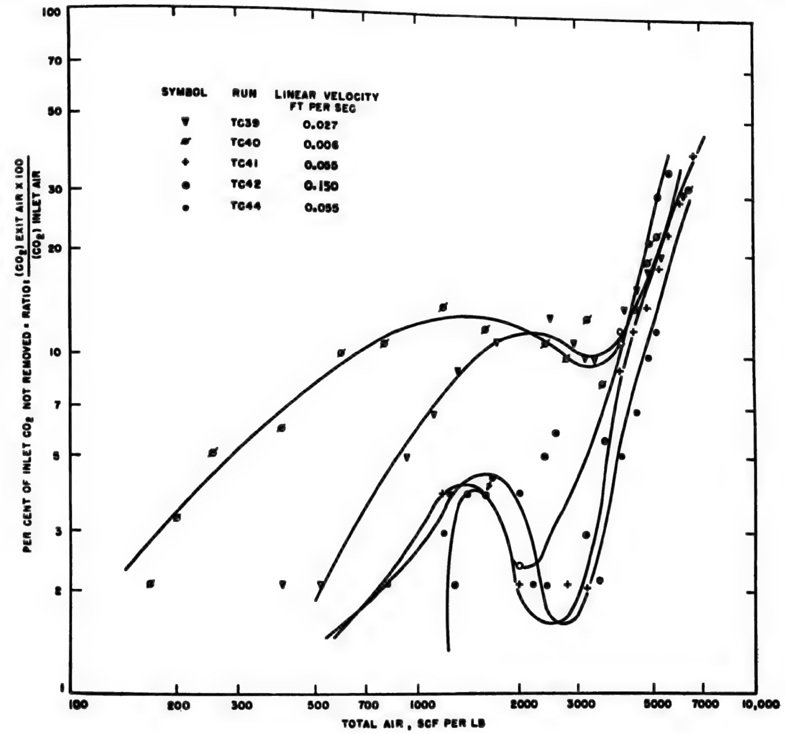


Figure 24. Effect of linear velocity on breakthrough.

"Life" Tests

"Life" is an arbitrary concept, depending upon the service for which the cleanup system is used. Here it is defined as the number of hours of operation which can be realized before the exit air contains 3% of the CO_2 concentration of the inlet air (with ordinary air, this critical concentration is 10 ppm CO_2). The *critical bed length* is a concept originally employed in studies on the adsorption of toxic gases on active adsorbents; in the present work it is defined as that length of adsorbent necessary, under given conditions of flow, temperature, pressure, and bed area, to reduce an entering concentration (C_0) of a contaminant (CO_2) to an arbitrarily chosen exit concentration ($C_E = 10$ ppm).

For the ends to which these studies were directed the runs at 3,000 psi are of the greater practical importance; the series of runs at 1 to 2 atm were made as a preliminary to the high-pressure runs and for the purpose of determining whether the methods of correlating results were applicable in both pressure ranges.

Life Runs at 1 to 2 Atmospheres. A series of runs were made at pressures corresponding to the pressure drop through the system with no exit throttling other than that provided by the flowmeter orifice. In

general this amounted to around 10 psi. The absorbent was 14 to 20 mesh; high-moisture soda lime and the small bomb were used.

These data were of interest in checking the validity of certain correlations of the data obtained in high-pressure runs; if such correlations hold for results obtained under two widely disparate sets of conditions they can be regarded with added confidence.

The low-pressure runs were made at three flow rates: 200, 400, and 600 scfh, and for each flow rate a series of runs with varying amounts of absorbent (that is, different bed length) were made.

In Figure 25 are plotted life-thickness curves for these flow rates, life being defined as *hours to 3% breakthrough*.

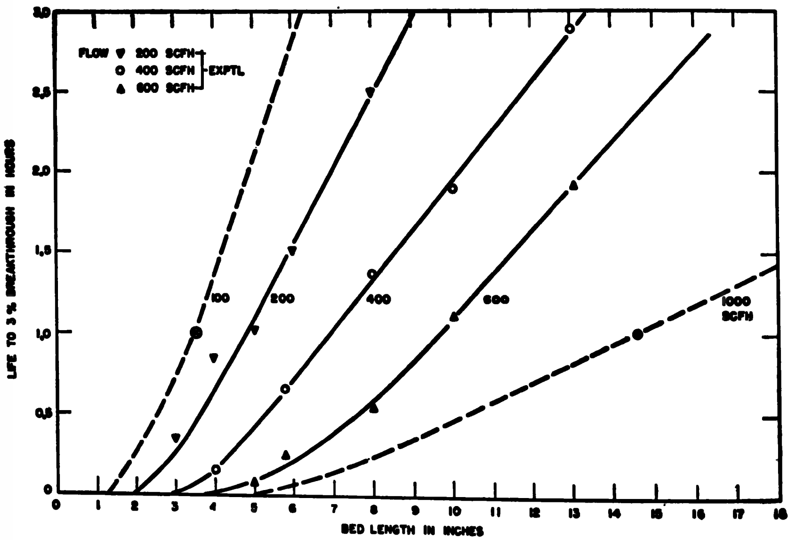


FIGURE 25. Life thickness curves.

Studies in Division 10, NDRC (Klotz, OSRD report No. 3774), have shown that in the adsorption of toxic gases on charcoal the following relationship exists between linear velocity and critical bed length.

$$\frac{F}{L_c} = KF^{-0.59} + K_1. \quad (3)$$

F = flow rate (proportional to velocity)
L_c = critical bed length

In Figure 26 is plotted F/L_c vs $F^{-0.59}$; it is seen that a straight line results. In Table 3 are given L_c values derived from Figure 26, those for 200, 400, and 600 scfh being the experimental values.

TABLE 3

F, scfh	L_c, in.
100	1.3
200	1.0
400	2.8
600	3.5
800	4.2
1,000	4.9

Life Runs at 3,000 psi. The life-thickness curves are plotted in Figure 27 (in which are included derived curves for 100, 800, and 1,000 scfh, with single data points for 100 and 1,000 scfh).

In Figure 28 are plotted critical bed lengths and pseudo-critical bed lengths vs flow rate. The pseudo-critical bed length is of somewhat greater usefulness than the true critical bed length, and is the intercept on the *length* axis of the straight-line portion of the life-thickness curve.

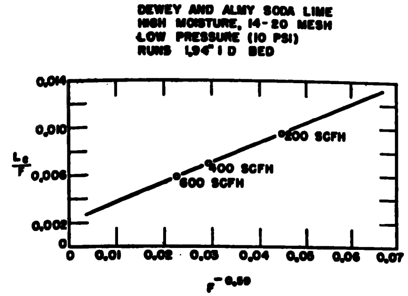


FIGURE 26. Effect of flow rate on critical bed length.

SLOPE OF THE LIFE-THICKNESS CURVE

The slope of the life-thickness curve is in the units, hours of life per inch of bed length. Thus it represents capacity of the soda lime, and if breakthrough always occurred at the same degree of exhaustion of the soda lime, the slope should be inversely proportional to flow rate. In Figure 29 are plotted the slopes of the straight-line portions of the curves of Figure 27 vs flow rate. It can be seen that at low flow rates the slope of the curve approaches minus one, but at higher rates it deviates considerably, indicating that the soda lime is utilized less efficiently at high rates of flow.

It is easy to calculate the position of the ideal curve shown as a dotted line in Figure 29, knowing the density and theoretical capacity of soda lime, as follows:

Slope of life-thickness curve (hr per in.)

$$= \text{density} \times \text{capacity} \times \frac{1}{F}, \quad (4)$$

where density = lb soda lime per in.³ = 53.5/1,728
capacity = scf air per lb soda lime = 12,000
F = scfh per sq in. bed area;

then

$$\text{slope} = \text{life (hr per in.)} = \frac{53.5 \times 12{,}000}{1{,}728\,F} = \frac{372}{F}.$$

Referring to Figure 29, it can be seen that the ideal curve shows life of 3.7 hr per in. at $F = 100$, exactly as the above calculation predicts.

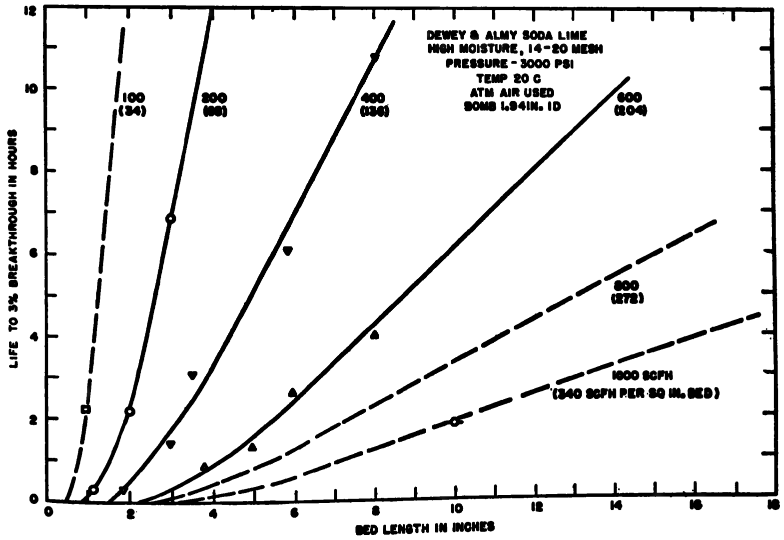


FIGURE 27. Life thickness curves.

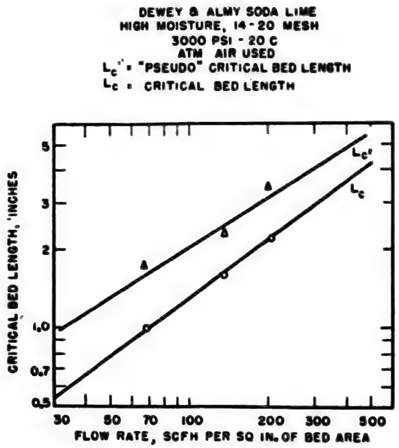


FIGURE 28. Pseudo-critical bed length.

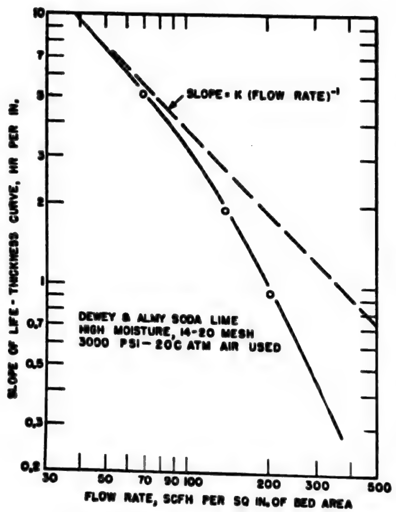


FIGURE 29. Effect of flow rate on life thickness.

The actual curve deviates from the ideal in a way that cannot be given a simple mathematical expression. It has been found that an approximation can be made which expresses the facts with reasonable accuracy (*ca* 5%) by considering the actual curve to consist of two straight lines of different slopes, intersecting at $F = 100$. The equations of these curves are:

For $F = 0$ to 100 scfh per sq in.,

$$\text{life (hr per in.)} = \left(\frac{310}{F}\right)^{1.07}. \quad (5)$$

For $F = 100$ to 300 scfh per sq in.,

$$\text{life (hr per in.)} = \left(\frac{200}{F}\right)^{1.69}. \quad (6)$$

The plot of Figure 30 is of further assistance in extrapolating the data. In this are plotted flow rate vs the lengths of bed required for a life of 10, 6, 4, 2, and 1 hr, respectively.

In Figure 32 are plotted life-thickness curves similar to those of Figure 28. It shows life-thickness curves with a greatly extended scale (up to 120 hr life and 18 ft of bed length).

It is not certain that extension of the data to such long bed lengths as in Figure 31 is entirely justifiable for high flow rates. It is, however, felt that reliance can be placed on this extrapolation for flows of 200 scfh per sq in. of bed area, or less. In any case, the values of life as chosen from a plot such as Figure 31 will be conservative; that is, a bed designed to last, say, 50 hr, will last at least that long (to 3% breakthrough).

The plot of Figure 32 was derived from the extended life-thickness curves of Figure 27. From this plot can be obtained the bed length necessary for operation for any required period, at a given flow rate.

The most striking conclusion to be drawn from the plots is that operation at a low linear velocity sharply increases the efficiency of utilization of the soda lime. For example, in a unit using a total air feed of 6,000 cfh (70 F), the use of a Harrisburg-type bomb (9.5-in. ID) allows about 85% of the *total* capacity of the soda lime to be used before 3% breakthrough, whereas the use of a 4.5-in. ID bomb allows only 29% of the total capacity to be utilized to the same point.

This result is to be expected from the observation noted in the preceding paragraph that the slope of

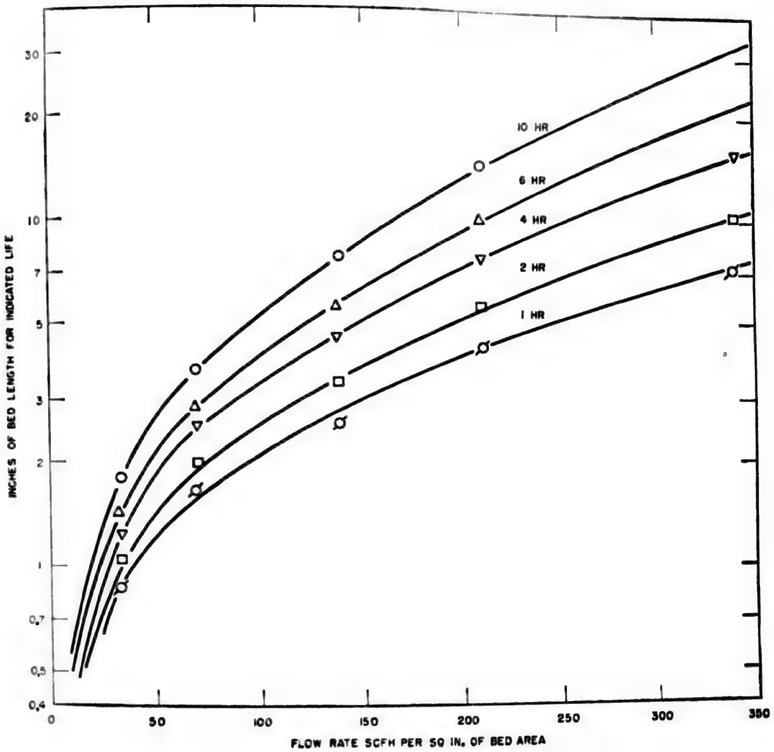


FIGURE 30. Bed length required under different operating conditions.

the life-thickness curve is inversely proportional to the flow rate at very low flows, but becomes inversely proportional to an increasing power of the flow rate at higher flow rates.

OTHER ABSORBENTS

In Figure 33 are plotted the results of a series of runs on several other absorbents: Wyandotte flake NaOH (TC 51); Niagara flake KOH (TC 65); Fisher pellet KOH (TC 52); Fisher pellet NaOH (TC 5[illegible]).

It is clear that 4- to 8-mesh soda lime is superior to any of these, and it can safely be assumed that 14- to 20-mesh soda lime would be greatly superior to any.

Baralyme. This is a proprietary name for a composition of 20% $Ba(OH)_2 \cdot 8H_2O$ and 80% $Ca(OH)_2$. It was tested at 3,000 psi, and found to be very inefficient under these conditions, being far inferior even to 4- to 8-mesh high-moisture soda lime. It can be concluded that soda lime, under the conditions used, particularly the 14- to 20-mesh high-moisture grade, is superior to any other alkaline absorbent studied. The reason for the relative ineffectiveness of KOH and NaOH may lie in the water relationships involved.[24]

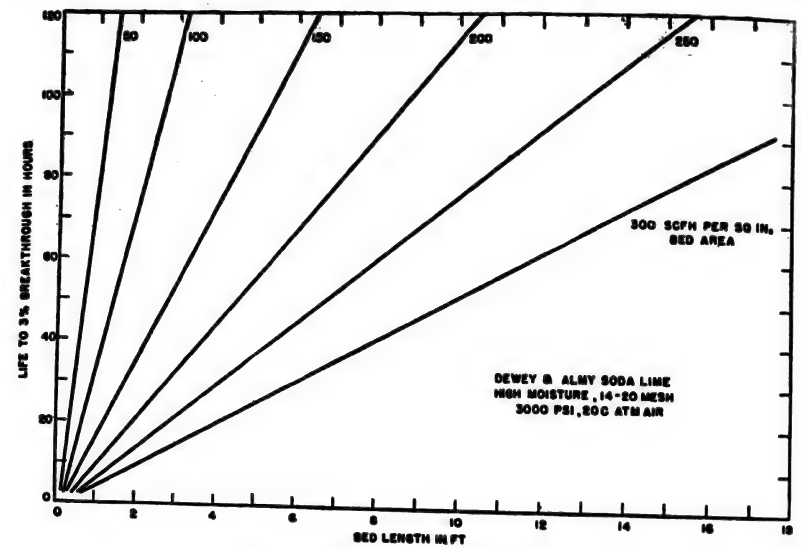


FIGURE 31. Expanded life thickness curves.

MOISTURE CONTENT

The most illuminative series of runs in this connection were on low-moisture soda lime (Figure 19).

The very dry low-moisture material allows about the same initial breakthrough for all flows from 400 to 1,600 scfh per lb. As the runs continue, however,

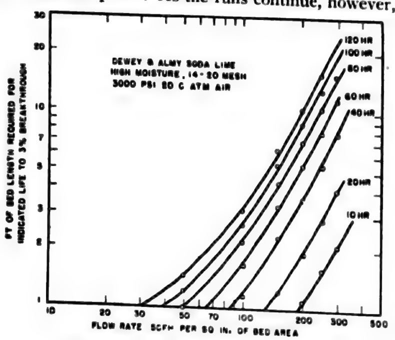


FIGURE 32. Bed length flow rate data.

water is formed and the soda lime becomes increasingly wetter. By the time the soda lime has become wet enough to attain maximum activity, however, it has absorbed a considerable amount of CO_2 and thus the curves never return to 100% removal and soon begin to climb towards complete exhaustion.

It can be seen from Figure 19 that the point at which the minimum is reached depends upon the total height of the curve. This means that in a run in which (because of a high flow rate) the stripping of CO_2 is quite incomplete, the amount of reaction to form water is likewise cut down so that a longer period of running is necessary to form the water necessary for maximum activity of the sodium hydroxide film.

The degree of exhaustion of the soda lime affects the overall rate of the reaction. This is shown by the fact that a group of breakthrough curves for different flow rates come together and become substantially coincident after 60 to 70% of the inlet CO_2 has passed through the bed.

The effect of the CO_2 concentration of the air being treated is shown by the curves of Figure 34.

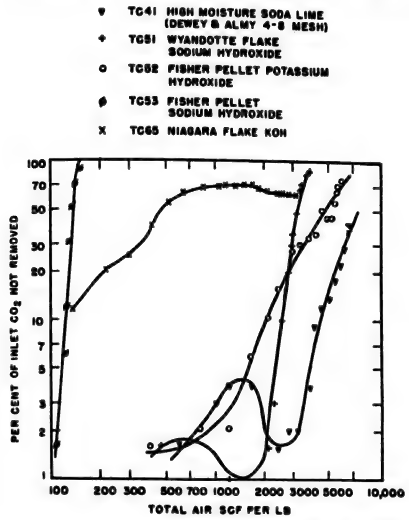


FIGURE 33. Break through curves for various absorbents.

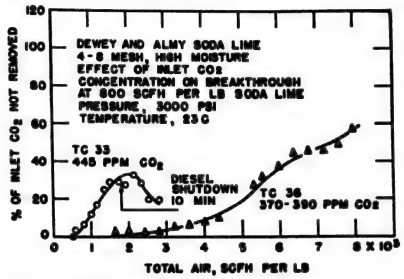


FIGURE 34. Effect of CO_2 concentration on breakthrough.

methods of temperature maintenance and control were chosen so as to simulate conditions which might be encountered if such a cleanup system were to be used on the Keyes unit (Chapter 4).

A series of runs on Columbia 4 ACW charcoal, 6 to 14 mesh, were made at different temperatures. The results of these runs are tabulated in Table 4.

It is apparent from these data that the saturation capacity of the charcoal is low and that rapid breakthrough occurs.

TABLE 4

Adsorbent: Columbia 4 ACW charcoal, 6 to 14 mesh.
Bed size: 0.953 in. ID by 10 in., containing 53.2 g charcoal.

Run number	9	8	10
Bed temperature F	−103	−147	−211
Flow, cfh (60 F, 1 atm)	39.3	39.7	41.0
Pressure, psi	2,450	2,500	2,500
Saturated adsorption, g CO_2 per g charcoal			
From adsorption data	0.0043	0.0052	0.0080
By desorption	0.0030	0.0057	......
Inlet CO_2 ppm	320	325	340
Max temperature on desorption, F			
Top of bed	−79	−80	−76
Bottom of bed	−21	−9	−16

These represent two runs made under identical conditions except for the higher CO_2 content of the inlet air in one run. It appears that in this case a transitory saturation of the surface of the particles has taken place, disappearing when added water is formed.

9.4.5 Adsorption of CO_2 on Active Adsorbents at Low Temperature

ADSORPTION AT 2,000 TO 3,000 PSI

The apparatus shown schematically in Figure 17 was used. This arrangement of apparatus and the

Run 13, using 104.2 g of activated alumina, with a bed temperature of −147 F at 2,500 psi and 45.6 cfh flow, showed complete adsorption for 20 min followed by steadily increasing breakthrough. The saturation capacity of the alumina was found to be 0.0142 g CO_2 per g. This is about three times the capacity of the Columbia 4 ACW carbon. As will be shown below, however, it is still low as far as practical usefulness is concerned.

Runs were made at −147 F, 3,000 psi, and about 40 to 45 cfh, using two other commercial charcoals. The saturation capacities are given in Table 5; a typical breakthrough curve is shown in Figure 35.

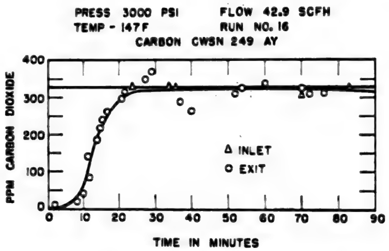


FIGURE 35. CO_2 absorption on activated carbon.

to make a rapid survey of a large number of substances.

Besides the various commercially valuable adsorbents on hand, the following materials were prepared.

Chromium Oxide. Two samples of this were made, one of which was clearly a gel, the other, duller in appearance, probably not gel-like in structure.

Chromium Oxide on Silica Gel. This is prepared by impregnating silica gel with chromium nitrate and precipitating the hydroxide in situ, followed by drying and heating.

Ferric Oxide. This is precipitated, dried, and heated.

TABLE 5

Adsorbent used: CWSN 249AY: 117 cc; 38 g
Columbia 6G: 117 cc; 52.5 g
Bed temperature: −147 F; pressure 3,000 psi; inlet air 325 ppm CO_2.

Run No.	Carbon	Saturation capacity, g CO_2 per g carbon: From ads data	By desorption
16	CWSN 249AY	0.0046	0.0053
17	"	0.0046	(0.0035)
18	"	0.0053	0.0066
19	Columbia 6G	0.0059	0.0058
20	"	0.0047	0.0053
22	"	0.0043	0.0054
24	Pittsburgh C. & I.	0.0067	......

TABLE 6. Adsorption of CO_2 from ordinary air at −78 C, atmospheric pressure.*

Material	Treatment	Number of runs	Adsorption† grams CO_2 per g
Silica gel	Pumped out at 200 C, 2 hr‡	3	0.0117
Silica gel impregnated with Cr_2O_3§	Heated at 300 C, 8 hr	4	0.0105
CWSN 249 AY carbon	As received	2	0.0081
Silica gel	As received	1	0.0080
Silica gel impregnated with Cr_2O_3§	Pumped out at 200 C, 2 hr‡	1	0.0069
Activated alumina	Pumped out at 200 C, 2 hr‡	2	0.0067
Columbia 4ACW carbon	As received	3	0.0065
Columbia 6G carbon	As received	2	0.0063
CWSN 291 AY carbon	As received	1	0.0063
Activated alumina	Heated at 180 C, 3 hr	3	0.0061
CWSN 17-6 carbon	As received	1	0.0060
Silica gel impregnated with Cr_2O_3§	Heated at 280 C, 4 hr	1	0.0057
Pittsburgh C. and I. Company carbon	Pumped out at 200 C, 2 hr‡	3	0.0054
Pittsburgh C. and I. Company carbon	As received	2	0.0050
Cr_2O_3 (gel)	Heated at 280 C, 4 hr	1	0.0032
Cr_2O_3 (precipitated)	Dried at 150 C	1	0.0024
Cr_2O_3 (gel)	Heated at 300 C, 2 hr	2	0.0008
Fe_2O_3 (precipitated)	Heated at 300 C, hr	2	0.0003

* Inlet air contained about 320 to 340 ppm CO_2.
† Saturation value. Runs continued at least 1 hr after analyses showed CO_2 concentration in exit air = CO_2 concentration in inlet air.
‡ Samples pumped out at full vacuum of Hy-vac pump.
§ Contained about 9% by weight of Cr_2O_3.

LOW-PRESSURE ADSORPTION AT −78 C

In view of the expenditure of time and materials necessary to complete successful high-pressure runs, a series of comparison runs were made at −78 C and atmospheric pressure. By this means it was possible

In Table 6 are given the results obtained, arranged in order of decreasing effectiveness. It is noteworthy that the saturation values obtained under these conditions are almost the same as those obtained at 3,000 psi and −145 F.

Examination of the values in Table 6 shows that most of the adsorbents tested are of about the same order of effectiveness. Silica gel appears to be the best from the standpoint of weight but it was not considered sufficiently superior to warrant the expenditure of time necessary to examine its breakthrough characteristics.

If certain assumptions are made, it is possible to estimate how much better an adsorbent has to be than those already tested in order for it to be of potential usefulness for the removal of CO_2 in a unit such as the Keyes unit. Taking run 16 (Table 5) as typical for active carbon, it is seen that breakthrough occurred almost at once and the carbon was saturated after about 40 min. In this run a space velocity of about 10,000 hr^{-1} (scfh per cu ft carbon) was used. The breakthrough curve for run 16 is reproduced approximately as curve OB, Figure 36.

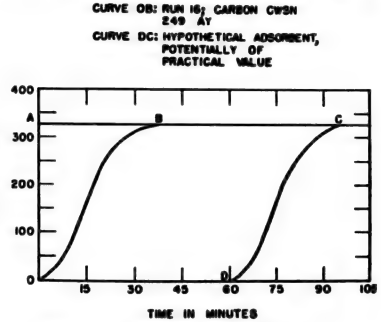


FIGURE 36. Time breakthrough curves.

USE OF DATA

The following will be assumed: (1) In a Keyes unit, the same space velocity will be used (2) with *complete* CO_2 removal, and (3) an adsorbent better than the carbon used in run 16 will show its superiority in increased time to initial breakthrough; that is, the slope of its breakthrough curve will not be less than that in run 16. Such an adsorbent would have the hypothetical breakthrough curve DC in Figure 36.

Referring to Figure 36, the total capacity of the carbon of curve OB is represented by the area CAB = 6.5 units. The total capacity of the absorbent of curve DC is represented by the area $OACD = 32.5$ units, five times the area OAB.

Thus it is seen that for an adsorbent to be worthy of consideration for use under the conditions specified above, it must have ***at least five times*** the capacity at saturation as the carbon of run 16 (CWSN 249 AY). Since it is probable that assumption (3) above is very conservative, it seems likely that an adsorbent must be well *over* five times better (in saturation capacity) than CWSN 249 AY to be operable under the conditions chosen. Since an adsorbent would tend to become less efficient on repeated cycling, it would probably be safer to assume that an adsorbent must be nearer ten times better than CWSN 249 AY to be satisfactory.

This calculation is admittedly an approximation but it furnishes the best basis upon which to answer the question: How can saturation values be used in selecting adsorbents of potential usefulness? It is clear that none of the adsorbents so far tested approaches the standard deemed necessary.

There is one further point which must be considered before discarding such adsorbents as the heavy metal oxides on the basis of low-pressure tests alone. One of the reasons for the low capacity of carbons at 3,000 psi may be the saturation of the active surface by nitrogen and oxygen. Unless CO_2 has a high *preferential* affinity for the adsorbent it is adsorbed to a small extent only. It was thought that metallic oxides, by virtue of a chemical combination rather than a physical adsorption, might show a high preferential adsorption of CO_2. This point is still unsettled at high pressures, but at low pressures no such preference is shown. In view of the requirements of a good adsorbent it was not deemed promising to pursue this point in more detail.

It can be concluded that no adsorbent has been found which is worthy of consideration for CO_2 cleanup in an operating unit of the Keyes high-pressure type.

9.4.6 Deposition of Carbon Dioxide from Air Streams by Direct Cooling

No information was available on the characteristics of solid carbon dioxide as precipitated from air streams. In the development of low-pressure oxygen producing units (Chapters 2 and 3) it was found possible to precipitate solid CO_2 at low temperatures and to evaporate the solid by reversing stream flows in a suitable manner. High-pressure units (see Chapter 4) were developed where the CO_2 was precipitated and removed from the air stream by filtration. Also, it was suggested[18] that the CO_2 content of submarine air could be controlled by precipitation of CO_2

by refrigeration. In all three applications it was necessary to obtain basic information on the equilibrium between solid and gaseous CO_2 and on the mechanisms involved in the precipitation and evaporation of CO_2.

Equilibrium between Solid CO_2 and Gaseous CO_2-Air Mixtures

In the design of air liquefaction-rectification equipment in which CO_2 removal is accomplished by condensation of the CO_2 as a solid it is important to have accurate data on the saturation concentrations of CO_2 in air over a wide range of temperature and pressures.

The use of existing data and known equations of state, such as van der Waals, Beattie-Bridgman,[24] is of value only under conditions which do not too closely approach those of the critical state; and the approximations made by assuming Dalton's law to hold (that is, that the mixtures are ideal) are only roughly valid at relatively low pressures and temperatures which are not too low. The conditions at which data are required (temperature below −100 C, pressure over 40 atm.) are beyond the range of validity of the fugacity rules of Lewis and Randal, using the van der Waals constants; and when the non-ideality of air only is taken into account by the use of Newton's empirical method the results are little better.

Calculations have been made using an adaptation of the method developed by Goff and Gratch, making use of a modified form of the Beattie-Bridgman equation, together with interaction constants whose forms were predicted by statistical mechanics. These calculations were far more successful than the van der Waals treatment.[23]

The applications of this technique are capable only of giving approximate indications of the order of magnitude of the deviations from Dalton's rule, and cannot be accepted for quantitative predictions to be used in the design of apparatus; they would have to be substantiated by experimental results. Since the calculated magnitude of the deviations seemed to be quite large in some cases, it was clear that it would be of great practical importance to study experimentally the saturation concentrations of CO_2 in air. These investigations would also be of extreme fundamental importance, since the available data on the property of gaseous mixtures are quite limited, so that additional data would be valuable for the future development of the theory of gaseous mixtures.

Analysis and Apparatus. The general principles of the method for CO_2 analysis have been described in preceding paragraphs.[24] The procedure consisted of condensation of the CO_2 (from a measured volume of sample air) in a coil immersed in liquid air or oxygen, evaporated into a closed titration vessel containing excess standard alkali, absorption by the alkali, and back-titration with standard acid.[17] As it was set up the method was suitable for CO_2 concentrations from 350 rpm down to 10 ppm or below, and was limited only by the necessity for taking large air samples for low CO_2 concentrations.[24]

The apparatus used is shown schematically in Figure 37. The essential part of the apparatus in the

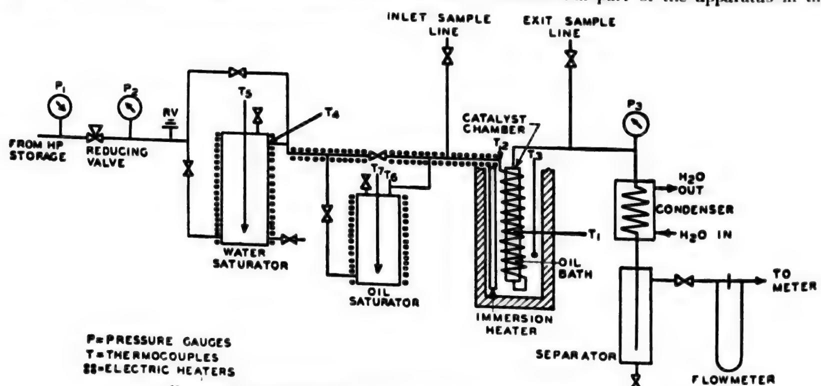


Figure 37. Flow diagram for deposition of carbon dioxide by cooling.

so-called equilibrium chamber is shown in Figure 38. This is constructed of heavy brass stock and contains an efficient filter composed of 6 layers of AA Fiberglas.

Experimental Procedure. After CO_2-free air is admitted to the equilibrium chamber and the selected flow established, the cooling air stream is adjusted and retained to give constant readings on T_3 and T_6. When T_1, T_9, and T_{10} reach a steady temperature the high-pressure air is passed around the soda lime scrubber and a run is started with an exit sample. Consecutive samples at the same temperature are given consecutive run numbers.

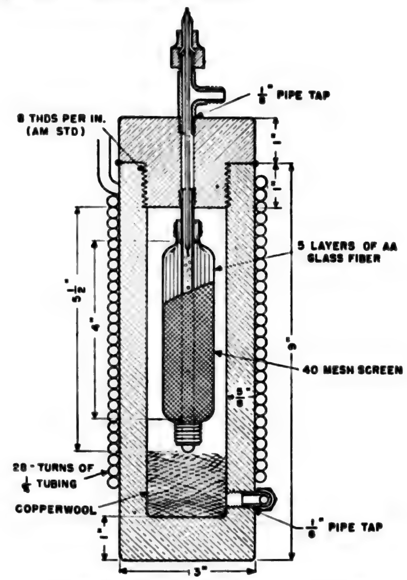


Figure 38. Carbon dioxide equilibrium chamber.

Control is directed to maintaining temperature equality in T_1, T_9, and T_{10} and to keeping these as close as possible to T_3 and T_6. Actually, when steady conditions have been achieved all these temperatures are very close to each other. T_1, T_3, and T_9 are measured on a potentiometer (±2 microvolts), while all other temperatures are observed on a Celect-Ray indicating potentiometer, the accuracy of which is probably not better than ±2 C.

Results. Preliminary experiments at 200 psi and temperatures in the range −130 to −150 C have been completed. These experiments had as their purpose a comparison of experimental results with the equilibrium concentrations calculated by means of various expressions involving empirical equations of state. It will be seen that the values calculated from the equations proposed are in good agreement with the experimental values. The results are plotted in Figures 39 and 40. The experimental points are connected by a straight line. To minimize subjective error, the experimental line was drawn first, after which the values derived from the equation were drawn in.

It can be seen that the experimental values are slightly higher than the Groff-Gratch values, except for three points at lower temperatures. In Figure 39 this difference amounts to about 0.3 to 0.8 C, the curves tending to be closer together at lower temperatures. This difference is inappreciable from a practical standpoint but is considerable from the point of view of the usefulness of the data as a basis for theoretical calculations.

It is felt that, if the divergence of the Goff-Gratch and the experimental values is due to an error in equilibrium temperature measurement, the error lies not in inaccuracy of T_1 but in the measurement of the *effective* equilibrium temperature. It was hoped to eliminate this uncertainty by using a massive equilibrium chamber and low flows through it. Whether the divergence is real or erroneous cannot be decided with certainty. It appears that the only way to get high precision and to answer this question would be to use a stirred liquid cooling bath and careful thermostatic control.

There is no doubt that the apparatus and procedure used are capable of considerable accuracy, however, and experiments were under way to gather data at higher pressures at the termination of this contract. Preliminary results indicate that even the Goff-Gratch approximation is grossly in error at 600 psi. Further work is continuing under Navy Contract NObs-2477 with the University of Pennsylvania.

Deposition of Solid Carbon Dioxide

One method for the removal of CO_2 from the atmosphere of a submarine (see Chapter 15) where a large supply of liquid oxygen is available, is to condense CO_2 as a solid by heat exchange.[18] The precipitated carbon dioxide, either deposited on the tube wall or filtered from the cooled air, could be evapo-

rated and discharged to the ocean by means of a vacuum pump.

A major uncertainty in the process lay in the type of deposit that might be obtained. No information was available to indicate whether the CO_2 would adhere to the walls of the cooling surfaces, be carried through the tubes as particles in suspension in the air, or be partly deposited and partly entrained. It was recommended that the first experiment in the investigation of a liquid oxygen refrigeration process should be directed toward finding the answer to this question.

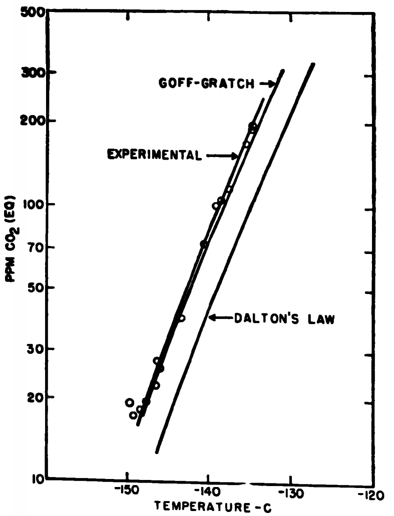


FIGURE 39. Equilibrium concentration of CO_2 and CO_2-air.

Other projects of the section had to do with the mechanism of CO_2 removal from cold air by precipitation before air liquefaction (see Chapters 2 and 3), and it was felt necessary to know more about how, when, and where CO_2 is deposited from a refrigerated air stream.

Under all conditions tried thus far, precipitated CO_2 adheres to the tube and apparently none of the solid leaves the tube as snow or particles in the exit air. A preliminary and qualitative approach to the second objective has been made, and some light has been shed on the probable mechanism of the CO_2 deposition process but the investigation of the quantitative relationships has barely started.

Because of the complete lack of knowledge of what might happen during the cooling of a stream of air and CO_2, several variables were considered in the initial design of the experimental unit. It was expected that the investigation would include study of the following variables: (1) concentration of CO_2 in the inlet gas stream, (2) velocity of gas flow, (3) temperature drop across cooling surface, (4) cooling by cold wall vs direct cooling by mixing refrigerated air with CO_2-rich air, (5) nature of surface; that is,

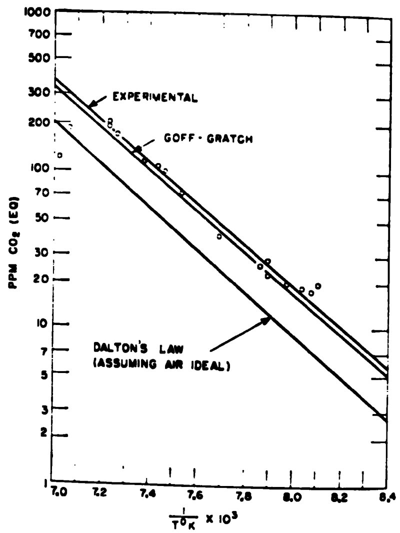


FIGURE 40. Equilibrium of CO_2-air.

whether rough or polished, and possibly the composition of the tube, (6) presence of baffles or other obstructions to flow, (7) shape of cross section of cooling surface, (8) use of centrifugal action, as in a cyclone filter, (9) density of gas, and (10) presence of crystals to act as nuclei for condensation.

Experimental Unit.[21] The original unit constructed to investigate CO_2 deposition is shown in Figure 41. It was somewhat elaborate, and was so constructed that the CO_2-air mixture could be directed either up or down through the tube; that either direct or indirect cooling could be used; and that any solid CO_2 not adhering to the deposition tube could be filtered.

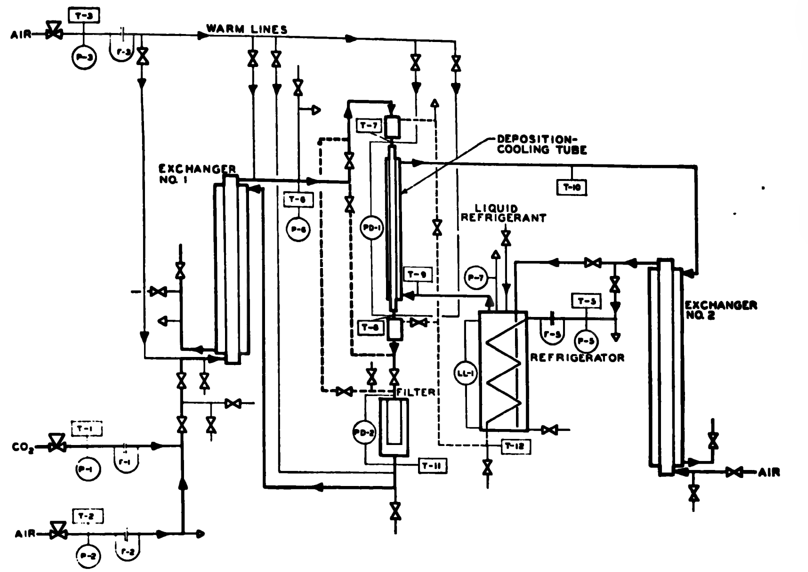


FIGURE 41. Flow diagram of experimental unit for study of CO_2 removal from air by refrigeration.

The solid lines in Figure 41 represent the usual flow of the air and refrigeration fluids. The dotted lines represent alternate flow paths. For example, the normal path of the air-CO_2 mix is through the inner annulus of exchanger 1 down through the deposition tube, through the filter and then through the outer annulus of exchanger 1. By using the dashed lines, the direction of flow of the mix can be reversed so the gas flows upwards through the deposition tube. By passing dry air from exchanger 2 through coils immersed in liquid oxygen, a controlled flow of cold air can be injected directly into the CO_2-air mix at either end of the deposition tube. Refrigeration is furnished by evaporating liquid oxygen. Dry air passes through the inner annulus of exchanger 2, bubbles through liquid oxygen in the refrigerated, and, with vaporized oxygen, flows through the outer shell of the deposition tube and through the outer annulus of exchanger 2. The several warm air lines shown in the figure are installed to provide means of warming the mix stream at critical points to vaporize CO_2 and determine the CO_2 deposition in various sections of the equipment.

The deposition tube is shown in Figure 42. It consists of ½-in. OD x ⅜-in. ID copper tube, wrapped with a single layer of 100-mesh copper gauze and inserted in a ¾-in. ID copper tube 5 ft long. The heat exchangers are Collins tubes (see Chapter 7), and the filter is a Porex filter tube, 2 in. in diameter and 6.5 in. long, positioned in a case constructed of a copper tube and streamline fittings.

Improved Unit. An improved unit[21] is shown in Figure 43. The essential difference between the units of Figures 41 and 43 are that the injection chambers, filter, warm air lines, and reverse flow lines were removed. An additional Collins tube was added to conserve refrigeration. Skin thermocouples throughout the unit were replaced by in-stream thermocouples. A heater was added at the exit of the deposition tube to vaporize any solid CO_2 that might issue from the deposition tube and thereby provide a homogeneous stream for accurate sampling.

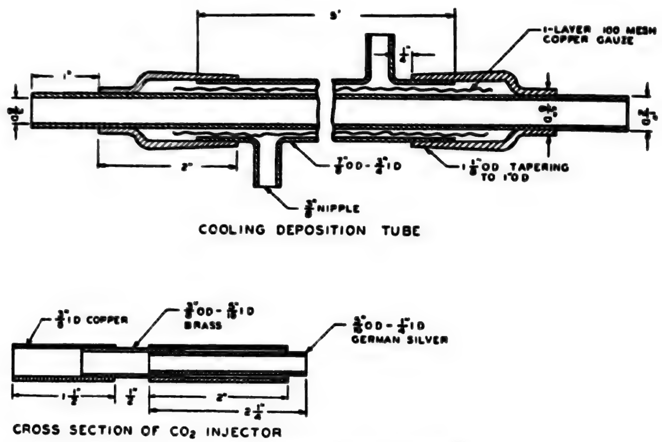


FIGURE 42. Carbon dioxide deposition tube.

The CO_2 system was changed. In order to prevent the deposition of CO_2 in the cooling exchangers, the CO_2 is now added to the cold air stream immediately after exchanger 1. Since this air would be at the dew point of 3% CO_2 (the desired temperature for the entrant air-CO_2 mix to the deposition tube), the problem was presented of injecting the CO_2 without plugging the injection line or having deposition in the line before the deposition tube. Therefore, a 50% CO_2-air mix is injected instead of pure CO_2. The presence of the air lowers the dew point and also makes more difficult the deposition of CO_2 in the injection line.

Even using the 50% CO_2-air mixture, the point at which this was injected would undoubtedly plug gradually and produce a continual decrease in amount of CO_2 being injected. To overcome this difficulty the injector shown in Figure 42 was devised. The purpose was to have the injection point without thermal contact with the main streamline. The injected stream, at room temperature, would keep the German silver tube warm enough to remain above the dew point of the 50% injection stream. The injector has worked quite successfully and shows no tendency to plug.

To overcome the effect of heat leak and also to obtain necessary adjustment of the temperature of the mixture entering at *T-7*, the line between exchanger 1 and the deposition tube (about 3 ft long) was encased to provide an outer annulus through which cold air from *T-3* (Figure 43), controlled in temperature with warm air from *T-11*, could be passed. With this arrangement it has been possible to maintain *T-4* and *T-7* at the same temperature.

The heat leak annulus would not be necessary if the CO_2 were injected immediately before the deposition tube. However, it is necessary to inject the CO_2 some distance before the tube in order to insure homogeneous mixing of the CO_2 and air before entering the deposition tube.

Control of the temperature and flow rates in the revised apparatus has been satisfactory although it requires very delicate manipulation of valves. The main difficulties of control are caused by (1) the heat capacity of the apparatus, which causes temperature reactions resulting from changes of flow rates to be quite sluggish, and by (2) the necessary frequent replenishment of liquid refrigerant, which causes a fluctuation in the temperature level of the cooling stream to exchanger 1.

Operation. To conduct a run, the unit is cooled to the desired operating temperature by means of liquid air in the refrigerator and by controlled flows of CO_2-free air. When the temperatures throughout have

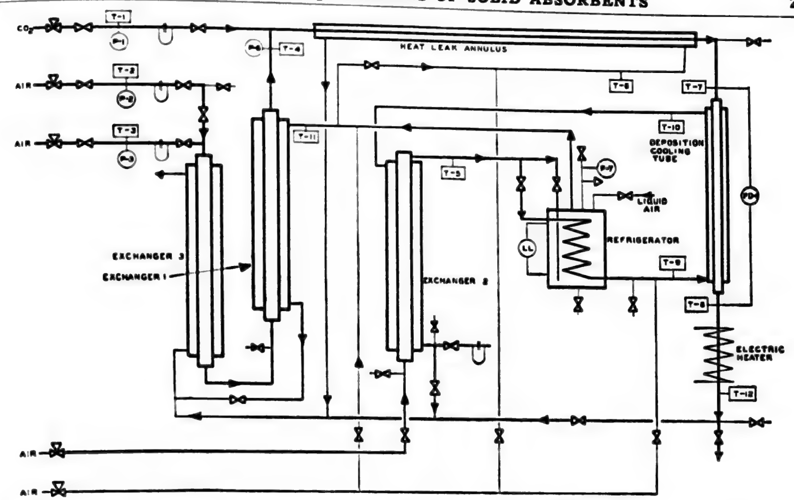


FIGURE 43. Flow diagram of improved experimental unit for study of CO_2 removal from air by refrigeration.

TABLE 7. Tabulated calculated data.

Run	Heat leak Btu per hr	Mix stream			Cooling stream			Deposited CO_2				
		Exit cfh	ΔT F	ΔH Btu per hr	Flow cfh	ΔT F	ΔH Btu per hr	lb per hr	*T-7* F	t_w F	*Q* dep Btu per hr	Diff Btu per hr
14	56.6	54.5	19	19.4	230	20	86	0.0672	−165	−185	17.2	7.2
19	43.7	162	18	54.5	224	27	113	0.066	−157	−177	16.8	2.0
20	47.0	161	18	54.0	240	27	121	0.1129	−162	−182	28.9	8.9
21	35.6	162	20	60.5	231	28	121	0.1193	−161	−181	30.6	5.7
24	37.8	161	26	78.4	248	36	167	0.2267	−165	−184	58.1	7.3
26	44.7	161	25	75.2	242	37	167.4	0.2267	−167	−185	58	10.5
27	33.2	162	33	100.0	250	42	196.2	0.2466	−163	−185	63.4	0.4
28	41.0	162	30	90.7	238	44	196	0.238	−172	−185	60.7	−3.6

reached steady conditions, the flow of 50% CO_2-air mixture from the storage cylinders is started, and the inlet concentration adjusted to that desired for the run. During operation the concentrations of the inlet and outlet streams are measured by an Orsat analysis. The pressure drop over the deposition tube is measured by a mercury manometer and the pressure difference recorded.

As shown in Figure 43, a heater was installed after the deposition tube to vaporize any CO_2 that might blow through the deposition tube; a homogeneous stream would thereby be obtained, insuring an accurate sample of the effluent stream. Conduction along the tube wall from the heater to the deposition tube adversely affected conditions at the cold end of the tube, so the heater was not used during the runs presented in the report.

As a run continues, the accumulation of CO_2 on the wall of the deposition tube causes a steady increase in pressure drop across the tube. The runs are terminated when the pressure drop reaches about 100 in. of water. The time required to reach this pressure drop is about 45 to 60 min.

Results. The data taken are summarized in Table 7. From the observed data enthalpy and material balances were determined and the average rate of CO_2 deposition calculated.

In the enthalpy balances the heat leak was deter-

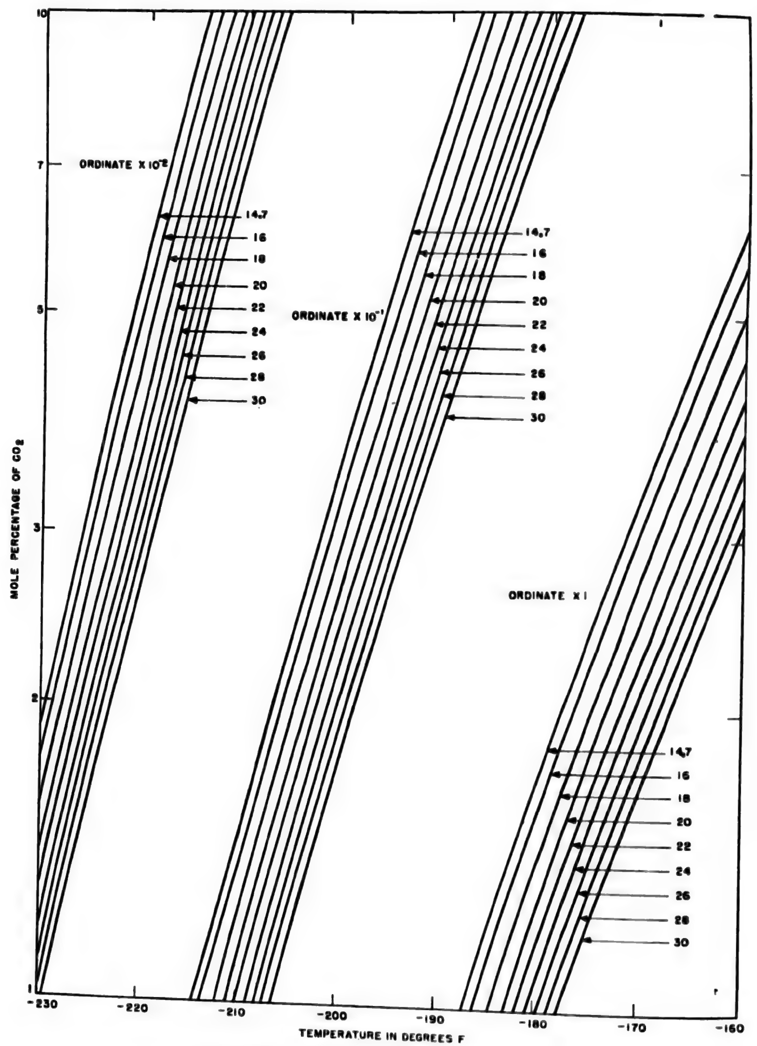


FIGURE 44. Saturation values of carbon dioxide in air.

tained for each run on the basis of data obtained while CO_2-free air was passing through the deposition tube) immediately before starting the injection of CO_2. In calculations of enthalpy balances for operation with the CO_2-air mix the heat leak was assumed to be unchanged from cooling of CO_2-free air and allowance was made for the enthalpy of precipitation of CO_2.

Discussion of the Results. The most significant fact disclosed by the data is that CO_2 was retained by the tube, and apparently not entrained in the exit gas. It is not possible to state that there is no CO_2 snow whatever in the leaving stream, because, with the present equipment, visual observation of the stream is not possible. The presence or absence of a small amount of solid CO_2 in the effluent is of academic interest, however, as the analyses of this stream give the total CO_2 content, both vapor and solid phase, and the essential fact is that the CO_2 in the leaving stream is less than that in the entering stream.

The most suggestive evidence on this point is obtained by comparing the exit CO_2 concentration with the dew point concentration under exit gas conditions. Figure 44 shows the saturation values of CO_2 in its mixture with air, at various temperatures and pressures. From the data of Figure 44, the saturation curve of Figure 45 was determined. The actual measured concentrations of CO_2 in the effluent streams are also plotted in Figure 45. If there were appreciable quantities of solid CO_2 in the effluent, the total CO_2 concentration, gas and solid, would be above the dew point concentration corresponding to exit conditions. Actually, all experimental points fall below the saturation curve, although their distance from the dew-point line is about equal to the experimental error. The analyses of CO_2 by means of the Orsat were probably accurate to 0.1 mole per cent. The temperature readings were taken from a Brown automatic potentiometer, and are probably correct to 1 F. Also, the thermocouple may read about 1 F too warm. The estimated errors are shown by the rectangles surrounding the data points of Figure 45.

Further evidence was obtained that in the usual experiments no appreciable breakthrough occurred but in one run, breakthrough did occur and was measurable. Such breakthrough occurred in no other run. However, in making run 26, a false start was made when CO_2 depositing in the line before the deposition tube made it necessary to warm the unit to remove the CO_2. As soon as there was no pressure drop across the tube, and apparently no CO_2 in the system, the run was restarted. It is quite likely that this procedure changed the surface characteristics of the deposition tube and resulted in the unusual breakthrough reported.

Heat balances, including allowance for the heat of deposition of CO_2, checked reasonably well, which also indicates that the CO_2 lost by the gas was actually retained as solid CO_2 by the tube. If solid CO_2 were precipitated and revaporized in the effluent after leaving the tube, enthalpy balances based on CO_2 deposition would be in error.

The data support the conclusion that CO_2 is solidified and deposited on the tube wall in amounts reasonably close to those to be expected from the dew point concentration of the effluent stream.

Because of CO_2 deposition on the wall of the tube, the pressure drop over the deposition tube steadily increased with time during each run. The pressure drop increases approximately exponentially with the weight of CO_2 deposited.[24]

Satisfactory quantitative calculations as to the mechanism and rate of deposition cannot be made from the data so far obtained. The thickness, density, and character of the deposit are unknown. Also, the tube wall temperature, which is a datum of fundamental importance, is unknown and not readily calculable. The overall Δt for heat transfer is not accurately known because of the uncertainty in the temperatures of the cooling fluid. Again, the 100-mesh screen in the annular space prevents an accurate calculation of the annular side heat transfer coefficient.

Process Requiring CO_2 Deposition. The results obtained in the experiments are favorable for the use of the direct cooling method for deposition of CO_2, as far as size of equipment is concerned. The results of the calculations show that as much as 0.24 lb per hr of CO_2 can be deposited on a single copper tube ⅜-in. ID, ½-in. OD and 5 ft long. To deposit 5 lb per hr of CO_2 (as would be necessary for a submarine) only 21 such tubes would be necessary. This number of tubes could be readily supported by a tube sheet 4 in. in diameter. No tube packing or special surface is required to insure the adhering of the CO_2 to the surface. The above tube dimensions were chosen arbitrarily at the beginning of the experiments, and are not necessarily the optimum for the purpose.

The practicability of the method will depend upon (1) the presence of liquid oxygen for refrigeration, (2) the space and weight requirement of auxiliary

equipment, and (3) the power requirement. The deposition unit itself seems to be practicable. The deposition unit would have to be constructed in duplicate to allow periodic vaporization CO_2. The optimum time cycle would depend on a balance between power requirements and the disadvantages of short cycles.

of these explosions; indeed, it can be said that no generalization on this point is possible, since local conditions probably play a decisive part in determining the causes which give rise to them.[24]

The explosions generally occur in those parts of the system which contain liquid oxygen, usually in the reboiler itself, but in at least one case on record, an explosion occurred in an entrainment separator through which passed vapor drawn from the reboiler. The violence of the explosions varies widely. Generally, the only result is the destruction of the reboiler and adjacent parts of the system without serious damage to regions outside the cold box or to operating personnel. However, violent explosions causing considerable damage have occurred, and the

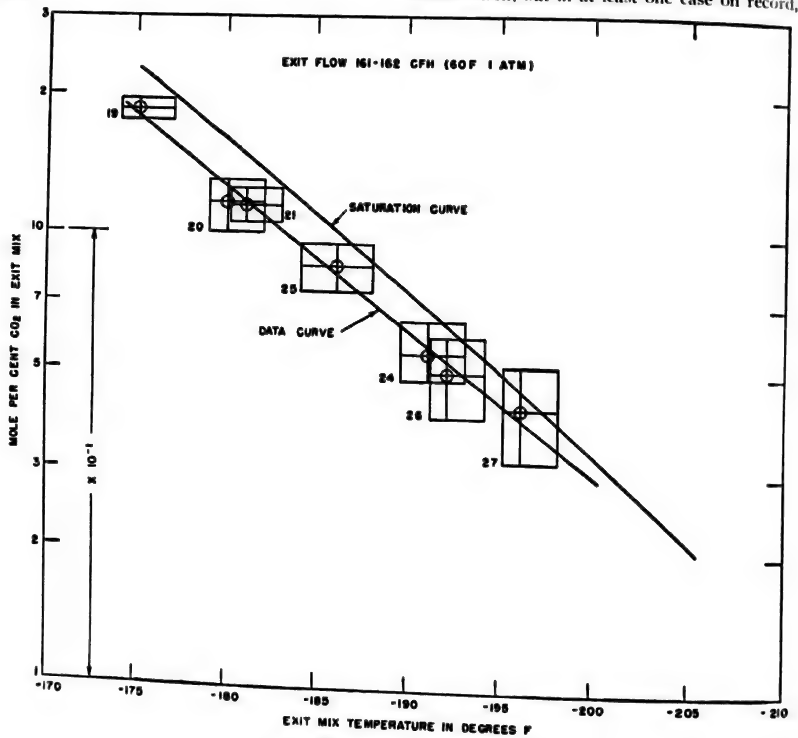


Figure 45. Exit CO_2 content vs temperature.

9.4.7 The Removal of Combustible Contaminants from Air

Danger and Causes of Explosions

The occurrence of explosions in oxygen producing plants is well recognized in the industry and occasional reports of such incidents occur in the technical literature. Little can be said concerning the frequency

danger of serious accidents must be considered always to be present.

There is not complete agreement as to the causes of explosions in oxygen plants. In general, however, it is accepted that the accumulation of solid acetylene in the presence of liquid oxygen is the important factor, although whether acetylene is initiary or contributory in its effect is not definitely certain.

The presence of hydrocarbons other than acetylene has also been suggested as an important factor, although it is not supposed that such substances are responsible for initiating explosions, but only that they are detonated by some other substance, such as acetylene or acetylides.

It has also been suggested that ozone may be responsible for setting off the explosion, possibly acting to detonate other substances such as acetylene or even saturated hydrocarbons. If ozone is responsible, it may act in conjunction with unsaturated hydrocarbons, forming the highly unstable ozonides, long known to be subject to explosive decomposition; or it may undergo spontaneous explosive decomposition, as it is prone to do when in the liquid state. Recent researches have shown that the ozone content of ordinary atmospheric air ranges around 0.02 ppm (depending greatly upon the locality and subject to wide fluctuations). The presence of ozone may be explained by the proximity of high tension wires and to the high static potential caused by friction of the driving belts of compressors as well as to the electrical charges arising from the passage of air through expansion valves; it is also produced in the atmosphere as the result of natural electrical phenomena.

When liquid oxygen is produced, the danger of explosion is relatively small since periodic withdrawal of some of the reboiler contents would prevent the accumulation of acetylene (and other hydrocarbons), unless these substances tend to precipitate as a film on the inner surfaces of the reboiler and thus not be removable as a suspension in the withdrawn liquid.

In a unit which produces gaseous oxygen the accumulation of acetylene and other hydrocarbons in the reboiler can proceed to an extent depending upon the intervals between which the equipment is warmed up for repairs, cleaning, etc. It is in this type of unit that the hazards are greatest, and most of the recorded examples of explosions which have occurred have been in gas-producing units.

No systematic methods of combating these hazards are in use in the oxygen industry. Certain precautions are frequently taken to prevent an explosion from causing injury to workmen or the extensive destruction of adjacent equipment. It is the custom in the industry to locate those pieces of apparatus liable to explosion in concrete pits or in exterior vessels fitted with blowout heads, and to drain the reboiler at frequent intervals.

Acetylene

The presence of acetylene and other hydrocarbons in air is probably caused entirely by such industrial operations involving the use and combustion of hydrocarbons, as the use of acetylene for welding, the operation of internal combustion engines, the use of oil for heat or power generation, etc.

Small amounts of hydrocarbon contaminants could conceivably be produced in the cylinders of oil-lubricated compressors, but there is no evidence that the temperatures attained in a compressor cylinder are high enough to cause any appreciable cracking of the lubricant.[27] It has been estimated, assuming a C_8 hydrocarbon, that if a temperature of 500 C were maintained in a cylinder for a long enough time to establish equilibrium in the reaction

$$C_8H_{18} \rightarrow C_6H_{14} + C_2H_2 + H_2,$$

a maximum of 0.3 ppm of acetylene would be formed, certainly an extreme upper limit not reached in practice.

The concentration of acetylene in air has been measured[26] and found to range between 0.01 to 0.1 ppm rising to as much as 2 to 3 ppm in the immediate vicinity of acetylene generating plants.

No information is available concerning the nature and concentration of other hydrocarbons in air. It is probable that in highly industrialized areas considerable amounts of low-molecular-weight hydrocarbons are present in the atmosphere. Liquid oxygen units operating in an industrialized section of Cambridge, Massachusetts, produce a liquid oxygen which is usually milky with suspended flocks of a suspended material which on examination has been shown to be of a hydrocarbon nature (but of unknown composition).

Analysis for acetylene in the reboiler of an M-7 type unit at the time when the liquid has just formed an insufficient quantity to fill the reboiler showed 0.2 ppm C_2H_2 present. It has been shown that if the entering air contains more than 0.04 ppm of acetylene, the latter can accumulate in the reboiler.[22] It is probable that hydrocarbons such as ethane, ethylene

and heavier hydrocarbons will accumulate at concentrations of the same order of magnitude, and the same is true of ozone (bp — 122 C) and nitrogen dioxide. Studies have been made as to the best methods for the removal of hydrocarbons and considerable work has been done on the removal of acetylene by adsorption on active charcoal, and by its catalytic oxidation to CO_2 and H_2O.

Catalytic Oxidation of Acetylene[22,24]

The compressors in use to supply air for air liquefying plants can be divided into two classes.

1. High pressure (3,000 psi).
   a. Oil-lubricated pistons.
   b. Dry pistons.
2. Low pressure (100 to 150 psi).
   a. Oil-lubricated pistons.
   b. Dry pistons.

The high-pressure compressors are usually four-stage compressors with the stage discharge pressures at 55 psi, 175 psi, 750 psi, and 3,000 psi respectively, with intercooling between each stage. The low-pressure compressors are usually two-stage compressors with intercooling between stages. The discharge conditions for the second compressor stage may vary from 348 to 359 F (176 to 182 C) for a discharge pressure of 107 psia.

It would seem possible therefore to operate a catalyst at about 100 psia and 300 to 350 F (149 to 172 C). There would be a choice of conditions in the high pressure compressor; that is, operation of catalyst at 55, or 175, or 750 psi.

The possibility of condensation of water on the catalyst during operation can probably be ruled out for any possible application.[22]

The pressure of oil in the air delivered by the compressor would of course depend upon whether the pistons were oil-lubricated or dry. The actual amount of oil carried through with the air would in any case depend upon the condition of the individual compressor, that is, type of oil, condition of rings, etc. The temperature of the oil delivered with the air would also depend to a great extent upon the individual compressor.

Catalysts of Interest Reported in the Literature. Much of the material of interest refers to the oxidation of carbon monoxide rather than acetylene. Many CO oxidation catalysts are also C_2H_2 oxidation catalysts, and the same promoters are often effective in both cases.

Interest in the problem of CO oxidation during World War I centered, at first, largely around chemical oxidants. Of the many oxidants tried it was found that a 1/1 mixture of MnO_2 and Ag_2O acted *catalytically*, not as a stoichiometric oxidant. This finding shifted the line of attack, which was thereafter directed at metal-oxide catalysts. In the course of the work on active preparation of $Co_2O_3 + MnO_2 + Ag_2O$ this mixture was found to be easily poisoned by H_2O; in fact, this sensitivity toward H_2O seemed to run parallel to the CO-oxidizing ability of the catalysts. The first agent actually made on a large scale for use in protective masks was 50% MnO_2 + 30% CuO + 15% Co_2O_3 + 5% Ag_2O, called Hopcalite I. Due to lack of time for basic tests, the familiar 60% MnO_2 + 40% CuO Hopcalite, which had already been prepared, was not tried in the field until later.

Further work has been done in NDRC, Division 10 on the oxidation of CO with Hopcalite and other agents.[13,24] Improvements were made in the methods of preparing MnO_2, so that gel-type Hopcalites could be produced which, in some cases, were superior to commercial MSA Hopcalite.[a] The addition of Ag_2O to MnO_2 had little effect, but a combination of $Ag_2O + MnO_2 + PdO$ was very active. Among the various Hopcalites, the ratio Mn/Cu often had less to do with the final activity than incidental variations in the preparative methods.

Promoters. In many of the catalyst preparations cited promoters were involved, though they were not sought for as such. Pd has been used as a promoter in a Cu catalyst for oxidizing a mixture of $H_2 + CO + O_2$. In a thoria catalyst for oxidation of CO, CeO_2 exerted optimum promoter action at a concentration of 0.96% which is also the best composition for ceriathoria gas mantles.

During World War I, while Hopcalite was being developed in the United States, British researchers were working on mixtures of CuO and MnO_2, with 1 to 5% CeO_2 as promoter for the oxidation of CO. Such mixtures as CuO + MnO_2, $Ag_2O + MnO_2$, CuO + Fe_2O_3, and the higher oxides of Ni, Co, or Fe with MnO_2 were found more active than the single oxides. Such catalysts were further improved by promoters, such as CeO_2, Pd, or Ag. The following quotation is especially significant in connection with the silver-Hopcalite catalysts used in our acetylene investigations.

[a] Product of the Mine Safety Appliance Co., Pittsburgh, Pa.

"Taking the CuO + MnO_2 mixture, and adding as a third constituent either ceria, cobaltic oxide, reduced metallic palladium, or silver oxide, the activity became much too great to compare with the previous results, by the method indicated."

Catalysts for Oxidation of Acetylene. Most of the catalysts for the oxidation of C_2H_2 listed in the literature were chosen specifically because they formed useful intermediate oxidation products, such as acetone, and acetaldehyde. Thus, the oxidations were incomplete and the concentrations of C_2H_2 used were exceedingly high compared with those of interest in the present study.

Russian investigations[22] were directed toward the oxidation of small quantities of acetylene, with the stated purpose (in some of the papers) of preventing explosions due to accumulation of C_2H_2 in the liquid oxygen of air-fractionating plants.

Present Experimental Investigation

The apparatus used, shown schematically in Figure 46, was constructed for the study of the removal of traces (1 to 10 ppm) of hydrocarbons (particularly acetylene) from air at 100 psi by means of catalytic oxidation.

Catalysts. The catalysts[24] used in the work can be divided into the following categories:

1. MSA Hopcalite.
2. MSA Hopcalite impregnated with Ag oxide and other Ag salts.
3. MnO_2 catalysts with and without additives such as CuO and Ag_2O, prepared here.
4. Gel Hopcalite furnished by R. N. Pease.[25]
5. Inert supports (silica gel and plaster of Paris) impregnated with Mn and other oxides.
6. Other catalysts.

Gases Used. All the catalytic runs made to date have been with air-acetylene mixtures containing 5 to 7 ppm of acetylene. The analytical method for acetylene is fully described[22] and the groundwork has been laid for work with other hydrocarbons.

As a typical light saturated hydrocarbon, butane was selected for the development of an analytical method to be used in connection with studies of the catalytic oxidation of substances other than acetylene. Concentrations of the order of a few parts per million are obviously beyond the range of standard gas-analysis equipment. The possibility of using a macromethod after condensation of the hydrocarbon in coils immersed in liquid O_2 or air using a Bureau of Mines-type Orsat apparatus was employed in the standardization of a butane mixture made up in a bomb. It was found that smaller gas samples could be taken if, instead of using the standard gas analysis apparatus, the condensed butane was burned and the CO_2 formed titrated by the special method reported previously.[17,24] The latter procedure was chosen for future application.

Conditions. All the experimental work on the catalysts was carried on at 100 psi with a flow rate of 50

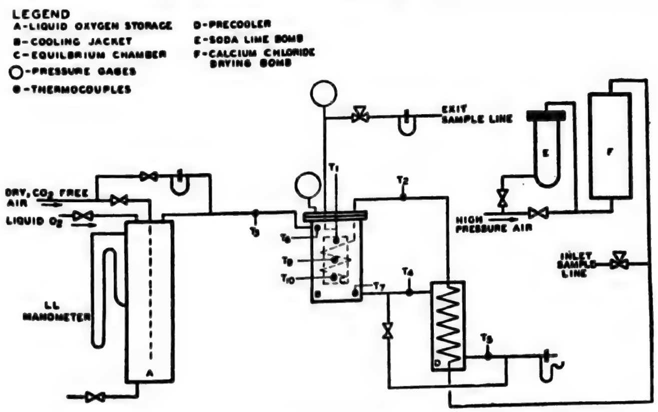


Figure 46. Apparatus for the removal of hydrocarbons from air by catalytic oxidation.

TABLE 8. Conditions: 200 F, 100 psi, 50 scfh, 25 cc, 16- to 20-mesh catalyst.

Run No.	Catalyst No. X-1-CO	Description of catalyst	ppm inlet	C_2H_2 exit	% Removal
		Group 1			
13	5	MnO_2-Ag_2O 6:4 (CEL)	5.2	0	100
14	8	MnO_2-Ag_2O 6:1 (CEL)	5.3	0	100
16	3	MnO_2-Ag_2O-PdO (Pease)	4.7	0	100
18	6	MnO_2-Ag_2O 6:2 (CEL)	6.1	0	100
20	13	MnO_2-Ag_2O gel 6:4 (CEL)	5.1	0	100
21	2	MnO_2-Ag_2O-CuO gel (Pease)	4.2	0	100
23	14	MnO_2-Ag_2O gel 6:4 (CEL)	4.3	0	100
25	16	MSA Hopcalite-Ag_2O (100:5) (CEL)	4.3	0	100
26	17	MSA Hopcalite-Ag_2O (74:7.4) (CEL)	4.7	0	100
32	22	Ag_2O on silica gel (CEL)	4.6	0	100
37	29	Ag_2O on silica gel (CEL)	5.1	0	100
51	39	MSA Hopcalite + Ag_2O on P. of P.* (10:1) (CEL)	5.6	0	100
52	41	MSA Hopcalite + Ag_2O on P. of P. (10:2) (CEL)	6.4	0	100
54	46	X-1-CO 39 activated at 250 C, 3 hr	6.4	0	100
55	51	X-1-CO 41 activated at 270 C, 3 hr	5.7	0	100
57	58	X-1-CO 7 activated at 250 C, 3 hr	5.7	0	100
60	67	X-1-CO 56 (MnO_2-Ag_2O on active C) activated at 250 C	7.1	0	100
		Group 2			
58	65	X-1-CO 50 (Hopcalite-Ag_2O-P. of P.) activated at 260 C	5.7	0.3	95
53	44	X-1-CO 3 activated at 250 C, 3.5 hr	6.4	1.2	81
59	66	X-1-CO 53 (SiO_2, Ag_2O, P. of P. activated at 250 C)	5.8	1.1	81
34	24	$KMnO_4$-$AgMnO_4$ on silica gel (CEL)	5.4	0.6	89
12	7	MSA Hopcalite impregnated with Ag_2O (CEL)	5.4	0.9	84
22	15	MnO_2-Ag_2O gel 6:2 (CEL)	4.0	0.8	80
24	15	MnO_2-Ag_2O gel 6:2 (CEL)	4.6	0.3	94
39	30	MnO_2-Ag_2O on P. of P. (CEL)	6.0	1.2	80
44	34	X-1-CO 30 activated at 210 C, 3 hr	5.9	1.7	71
40	31	MSA Hopcalite activated at 200 C, 1.5 hr	5.7	2.0	65
15	1	MnO_2-CuO 2:1 (Pease)	5.3	2.2	59
11	12A	MSA Hopcalite as received	4.9	2.3	53
19	11	MnO_2-CuO 6:4 (CEL)	6.1	3.1	49
49	43	X-1-CO 10 activated at 250 C, 3 hr	5.6	2.6	54
50	42	X-1-CO 11 activated at 250 C, 3 hr	5.6	3.2	44
		Group 3			
33	23	CuO-Ag_2O on silica gel (CEL)	4.8	3.3	31
17	10	MnO_2-CuO gel 6:4 (CEL)	4.7	3.6	23
43	27	$KMnO_4$-$AgMnO_4$ on P. of P. (CEL)	4.8	4.0	20
36	26	Ag_2O on P. of P. (ppt'd in situ) (CEL)	4.7	3.8	19
29	4	Davso Platinized silica gel	4.6	3.9	15
27	18	MSA Hopcalite-CuO-H_3PO_4	5.2	4.7	9
28	19	Baker Tech. (85%) MnO_2	5.2	4.8	8
8	12B	MSA Hopcalite wetted, dried at 110 C	5.3	4.7	11
		Group 4			
30	20	Silica gel	4.6	4.6	0
31	21	Cr_2O_3 (9%) on silica gel (CEL)	4.8	4.8	0
41	35	CWSN 249 AY carbon	5.9	5.9	0
42	36	Salcomine	5.4	5.4	0
36	25	MnO_2-Ag_2O on silica gel (CEL)	4.7	4.7	0

Note. Exit analyses are averages of two simultaneous, parallel samples. Inlet analyses are generally averages of several single samples. With few exceptions, averages of analyses of same sample generally check individual results within ±0.2 ppm.
* P. of P. = Plaster of Paris.

scfh and a catalyst volume of 25 ml. This is equivalent to a space velocity of 50,000 hr^{-1} (all space velocities reported herein are referred to standard conditions; that is, sv = scfh per cf catalyst volume). The air-acetylene mixtures were made up in Harrisburg bombs and pressured up to 3,000 psi. The C_2H_2 concentration was 5 to 7 ppm. Experimental runs were carried out under three different sets of conditions: dry mixture, water saturated mixtures, and water- and oil-saturated mixtures.

The dry runs were made at a catalyst temperature of 200 F. This was chosen because the catalyst which was chosen as a standard, MSA Hopcalite, gave 53% removal under these conditions and therefore would serve as a good basis for comparison.

graded Hopcalite-Ag_2O catalysts was also run to determine the minimum silver oxide necessary for complete acetylene removal under these conditions. The results of these runs are given in Table 9.

Two runs were made at a catalyst temperature of

TABLE 9

Conditions: 300 F, 100 psi, 50 scfh, 25 cc, 16- to 20-mesh catalyst, water-saturator at 150 F.

Run No.	Catalyst No. X-1-CO	Description of catalyst	ppm inlet	C_2H_2 exit	% Removal
61	5	MnO_2-Ag_2O 6:4 (CEL)	6.3	0	100
66	6	MnO_2-Ag_2O 6:2 (CEL)	5.5	0	100
67	13	MnO_2-Ag_2O gel 6:4 (CEL)	5.5	0	100
64	29	Ag_2O on silica gel (CEL)	6.2	0.3	95
65					
75	39	MSA Hopcalite + Ag_2O on P. of P. (10:1)	6.2	0	100
72	72	MSA Hopcalite + 5% Ag_2O (CEL)	5.6	0	100
73	73	MSA Hopcalite + 10.0% Ag_2O (CEL)	5.8	0	100
68	16	MSA Hopcalite + $AgMnO_4$ (100:5) (CEL)	5.6	0	100
62	8	MnO_2-Ag_2O 6:1 (CEL)	5.5	2	96
63	12A	MSA Hopcalite	6.2	3	95
69	69	MSA Hopcalite + 0.1% Ag_2O (CEL)	6.2	2.1	66
70	70	MSA Hopcalite + 0.5% Ag_2O (CEL)	5.8	1.6	72
71	71	MSA Hopcalite + 1.0% Ag_2O (CEL)	5.8	1.9	67
74	69	X-1-CO 69; Act. 3.5 hr 250 C	5.8	0.8	86
			5.6	1.2	79

The water-saturated runs were made at a catalyst temperature of 300 F and a water saturator temperature of 150 F.

The water- and oil-saturated runs were made at a water-saturator temperature of 150 F and at oil-saturator temperatures of 150 F, 225 F, 275 F, and 300 F.

Experimental Results. The first 60 runs were made at 200 F, 100 psi, using dry (that is, saturated at 2,500 psi) mixtures of air-acetylene (6 to 7 ppm).

The results of these runs are given in Table 8. They are grouped in four classes: (1) runs in which no acetylene was detectable in the exit gas; (2) runs in which removal was less than 100% but better than 50%; (3) runs in which some removal was observed; and (4) those in which no removal was effected.[24]

It will be seen that the first group includes, without exception, only catalysts containing silver oxide. Without exception, catalysts which do not contain silver remove less than 65% and catalysts which are not Hopcalite or Hopcalites plus Ag_2O are quite ineffective.

The water-saturated runs were made with a catalyst temperature of 300 F, a water-saturator temperature of 150 F, at 100 psi and using air-acetylene mixtures of 5 to 7 ppm concentration and MSA Hopcalite was run as a basis for comparison. A series of

200 F further to separate the 5% and 10% Ag_2O on Hopcalite. These data are given in Table 10.

TABLE 10. Conditions: catalyst temperature 200 F, 100 psi, 50 scfh, water-saturator temperature 150 F.

Run No.	Catalyst No. X-1-CO	Description of catalyst	ppm inlet	C_2H_2 exit	% Removal
78	12A	MSA Hopcalite	5.3	5.3	0
76	72	MSA Hopcalite + 5% Ag_2O	5.6	0.8	86
77	73	MSA Hopcalite + 10% Ag_2O	5.6	0	100

From these data, it would seem that a 10% Ag_2O on MSA Hopcalite would be a likely choice for further work with water- and oil-saturated air-acetylene mixtures.

A series of runs was next made with water and oil saturation, with oil-saturator temperatures of 300, 275, 220, and 150 F. The results are given in Table 11.

The difference between catalyst No. X-1-CO-73 and X-1-CO-73-B was only in the method of grinding before pelleting and mashing. X-1-CO-73 was ground in a mortar and pestle wet, whereas X-1-CO-73-B was ground dry in a ball mill.

In an effort to determine the effectiveness of the Hopcalite-Ag_2O (10%) catalyst in burning the oil coming from the oil saturator, the amount of vola-

tilized and the amount burned were determined on separate runs in three temperature regions.

The volatilized oil was condensed in a coil similar to that used in the acetylene analysis method except for the addition of an AA Fiberglas filter. This coil, which was located in place of the usual catalyst bomb, was cooled with liquid oxygen. At the end of each run, the condensed oil was removed from the coil with acetone and carbon tetrachloride. The solvents were evaporated and the oil weighed.

For analysis of oil burned, it was decided to determine CO_2 in exit samples from the unit during regular C_2H_2 runs, using the procedure of condensing the CO_2 in coils and allowing it to expand into the titration vessel. These analyses were subject to two sources of contaminant CO_2: the content of the inlet air, and the CO_2 resulting from the oxidation of C_2H_2 on the catalyst. Correction was made for the former by CO_2 analysis of the inlet air (from which the CO_2 was largely removed by the insertion of a soda-lime scrubber on the high-pressure side), and for the latter by converting the inlet C_2H_2 analyses to ppm CO_2 (in these runs the oxidation was 100%). The corrected CO_2 values were then converted to grams of oil per standard megaliter of air, considering the oil to be composed of 85% carbon. The results are given in Table 12 and Figure 47.

At an oil-saturator temperature of 275 F, about 60% of the oil was burned, at 220 F about 83%, and at 150 F over 100%. This last result was probably due to the error in extracting and weighing a quantity of oil in the range of 70 mg, as well as to the observed phenomenon that the heated oil released hydrocarbons which were gaseous at room temperature but condensable at the temperature of liquid O_2. These would be included in the burned-oil but excluded from the volatilized-oil measurements, thus appreciably affecting the results at low oil levels.

Conclusions. From the experimental data it is apparent that it is possible to remove acetylene (ca 5 to 7 ppm) from an air-acetylene mixture at conditions approximating those to be found on the discharge side of a low-pressure (100 psi) compressor or after the first or second stage of a high-pressure (3,000 psi) compressor. It has been shown experimentally by others that the efficiency of MnO_2 and of CuO increased with decreasing concentrations of acetylene. Inasmuch as acetylene concentrations under actual operating conditions average 0.01 to 0.1 ppm (and may go as high as 2 to 3 ppm under extreme conditions), it is not unreasonable to assume that the Hopcalite + 10% Ag_2O catalyst will be more efficient with lower concentrations of acetylene than we have shown with 5 to 7 ppm.

From the data it would seem that 10% Ag_2O on Hopcalite would be enough silver as a promoter to do a good job. However, actual life tests would be necessary to support this assumption.

It has also been shown that from 60 to 100% of the oil in the air stream (depending upon the temperature of the oil saturator) is burned on the catalyst together with the acetylene.[24]

The following projects were unfinished at termination of the NDRC contracts. Further information may be obtained under Navy contract Nobs 4777.

1. The life of the catalyst using dry air-acetylene mixtures.
2. The life of the catalyst using water saturated air-acetylene mixtures.
3. The life of the catalyst using water and oil saturated air-acetylene mixtures.
4. The removal of hydrocarbons other than acetylene for example, propane and butane.
5. Methods of reactivating a catalyst grown inactive in use.
6. Addition of promoters other than silver, for example, CeO_2.

TABLE 11

Conditions: catalyst temperature 300 F, 100 psi, 50 scfh, 25 cc, 16- to 20-mesh catalyst, water-saturator temperature 150 F, oil-saturator temperature as indicated.

Run No.	Catalyst No. X-1-CO	Oil-saturator temperature	Description of catalyst	ppm inlet	C_2H_2 exit	% Removal
79	12-A	300 F	MSA Hopcalite	6.5	6.5	0
80	73	300 F	MSA Hopcalite + 10% Ag_2O (CEL)	6.1	1.9	70
86	73-B	300 F	MSA Hopcalite + 10% Ag_2O powdered in ball mill before pelleting (CEL)			
87	73-B	225 F	MSA Hopcalite + 10% Ag_2O powdered in ball mill before pelleting (CEL)	6.0	0.4	93
81	73	220 F	MSA Hopcalite + 10% Ag_2O (CEL)	5.3	0	100
83	39	220 F	MSA Hopcalite Ag_2O (6:4:1) (CEL)	6.1	0	100
84	22	220 F	Ag_2O on Silica gel (CEL)	5.3	0	100
82	73	150 F	MSA Hopcalite + 10% Ag_2O (CEL)	5.9	0	100
				4.7	0	100

TABLE 12

Oil temperature	Oil volatilized	Oil temperature	Oil burned
275 F	162		
	168 g per 10^6 liters	275 F	97.3 g per 10^6 liters
220 F	50.0 g per 10^6 liters	221 F	41.3 g per 10^6 liters
150 F	7.7 g per 10^6 liters	152 F	12.3 g per 10^6 liters

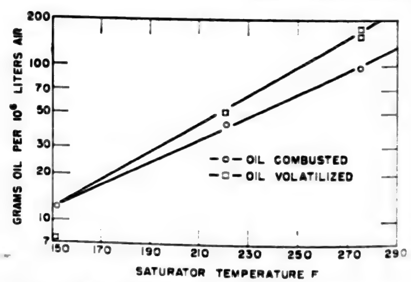


FIGURE 47. Amount of oil vaporized and burned in relation to the oil saturation temperature.

Chapter 10

MISCELLANEOUS EQUIPMENT

By *J. H. Rushton*

10.1 INSULATION

The efficiency of liquid air fractionation plants is strongly dependent on the effectiveness of the thermal insulation enclosing the low-temperature portions of the plant. For the mobile and air-transportable plants it is desirable to use an insulating material that is both highly effective and light in weight. An evaluation of various materials could not be made on the basis of available information, and therefore some experimental tests were required.

Tests were made[2] on thirteen different materials at one or more densities in the range of 2 to 14 lb per cu ft. Results are given in Table 1. All tests were made under similar conditions in the same apparatus. The criterion of insulation quality was the total heat transfer through the insulation.

The apparatus used consisted of a tube 6 ft high by 4 in. OD, supported in a rectangular box 7 ft high by 20 in. square. The insulation to be tested was packed around the tube, filling the free volume of the box. The tube was filled with liquid air and the heat flow through the insulation was measured indirectly by the rate of evaporation of the liquid air after the apparatus had been cooled to equilibrium temperatures.

Characteristics of the three outstanding insulations are given in Table 2. Fiberglas shoddy from mixed yarns and scrap from forming, twisting and plying operations, proved to be the best insulation material for use in mobile oxygen units. Santocel insulation was superior to this Fiberglas in that it had a lower heat transfer, but the Santocel powder is undesirable since it can be lost from a unit by being blown from the cold box as a result of a break in the high-pressure apparatus. It is possible that packing the Fiberglas to about 8 lb per cu ft might make it as effective as Santocel at its normal density of 7.4 lb per cu ft.

Dry Zero kapok insulation was the lightest of the effective insulations, but its effectiveness was probably due to its manner of installation. Paper backing on the material was used to form vertical and horizontal convection current barriers. This method of application would be impractical in oxygen units. No test on this material in bulk form was made.

An optimum density was not found for any insulation in these tests. In all cases the insulating effectiveness improved with increasing density up to the highest densities used. Other similar tests[3] on various types of glass wool showed optimum densities ranging from 5 to 8 lb per cu ft, but the insulation thickness used was only about 4 in., compared to the 8-in. thickness used in the more comprehensive tests. The optimum density for any insulation is probably a function of insulation thickness, temperature difference, and size, shape, and orientation of the insulated system.

For low-cost insulation when weight is not of importance, rock wool should prove most suitable since this is almost as effective as the more expensive materials.

10.2 FILTERS

The use of special filters has been required in some NDRC oxygen plants for (1) the removal of fine oil particles from the compressed air fed to the separation system, and (2) the removal of solid carbon dioxide particles from liquid air streams.

The complete removal of oil from the compressed-air feed was first found necessary in the low-pressure M-7 unit. The small amount of oil passing through conventional air separators seriously fouled the reversing exchangers within several days of operation. The use of gas-mask asbestos paper[4] proved quite successful in removing the extremely fine oil particles that could not be removed by conventional means. In the design of filters using this paper, air velocities of 10 ft per min or less are used, with 8 to 12 layers of paper. The paper is usually wound on long tubes with the gas flow being radial inward, and a sufficient number of tubes in parallel is used to obtain the necessary filtering area. The oil particles are retained in the porous paper, and the paper must be replaced periodically. The life of the paper obviously depends on the amount of oil passing the preliminary separators and filters used.

Fiberglas AA mat, phenol formaldehyde treated, has proved about as effective as the asbestos paper.

TABLE 1. Summary of results

Insulation	Density lb per cu ft	Per cent‖ moisture	Heat leak† (0% evap.) Btu per hr	ΔT_{top}‡ F	ΔT_{mid}‡ F	ΔT_{Btm}‡ F	Run No.
1. Rock wool* (white)	11.6	0.0	300				1-B
	11.6						1-C
	12.2						1-D
2. Fiberglas T.W.F.	2.0	0.1	940				
	3.4		780	4	1	37	2-A
	6.1		430	5	2	21	2-C
	8.3		320	3	2	12	2-D
3. Fiberglas bulk silk "E"	4.4	0.0	440	2	0	26	3-A
	5.7		290	4	3	14	3-B
4. Fiberglas semi-rigid batts	4.2	0.1	1,220	4	19	28	4-A
	5.7		450	3	2	..	4-B
	5.7		450	2	3	30	4-C
5. Fiberglas continuous shoddy	2.9	0.4	750	1	1	42	5-A
	5.3		480	3	0	26	5-B
	7.4		350	3	1	15	5-C
	8.8		350	3	1	14	5-D
6. Santocel	7.3	3.1	174	0	0	0	6-A
7. Eagle Picher 7-B granulated wool	9.7	0.0	325	2	2	7	7-A
8. Fiberglas garnetted shoddy	5.5	5.4	570	0	2	27	8-A
9. Fiberglas heat cleaned bulk cotton	4.54	0.1	405	1	1	19	9-A
10. Johns-Manville rock wool	9.1	0.9	375	3	3	11	10-A
	13.3		345	2	1	6	10-B
11. Ferrotherm	14.1		570	2	4	10	11-A
12. Dry Zero	1.9	16.1	310	2	3	16	12-A
13. Fiberglas shoddy§	5.8		270	..	..	..	13-A

* The score of this material is not known and hence it cannot be definitely identified.
† Extrapolated value.
‡ ΔT's Subscript denotes elevation. Values given are average values of ΔT between surface temperature and air temperature at center and edges of box.
§ Fiberglas shoddy from mixed yarns and from forming, twisting and plying operations.
‖ This moisture content is merely an indication of how susceptible the various materials are to picking up water. *The moisture content of the insulation used in the heat leak tests may have been different.*

TABLE 2. Characteristics of the three best insulations.

	Fiberglas shoddy*	Santocel	Flameproof Dry Zero
Heat leak, Btu per hr	270	175	310
Density, lb per cu ft	5.8	7.4	1.9
Durability	Good	Probably good†	Not wetted by water
Inflammability	Does not burn	Does not burn	Burns in oxygen Does not burn in air
Facility of application	Fairly easy	Easy	Difficult

* From mixed yarn and scrap from forming, twisting and plying operations.
† Detrimental feature is that it can be lost from cold box if leak occurs in unit.

However, no direct measure of filtering efficiency has been attempted with either material.

The filtration of solid CO_2 particles from liquid air streams proved to be no more difficult than conventional filtration of solids from liquids. However, CO_2 is soluble in liquid air to the extent of several parts per million, and of course this dissolved amount could never be removed by filtration.

Experience showed that practically all the CO_2 in excess of solubility could be filtered out by commercial glass filtering cloths of the finest grade or by Fiberglas AA mat.[5] The filter cake could readily

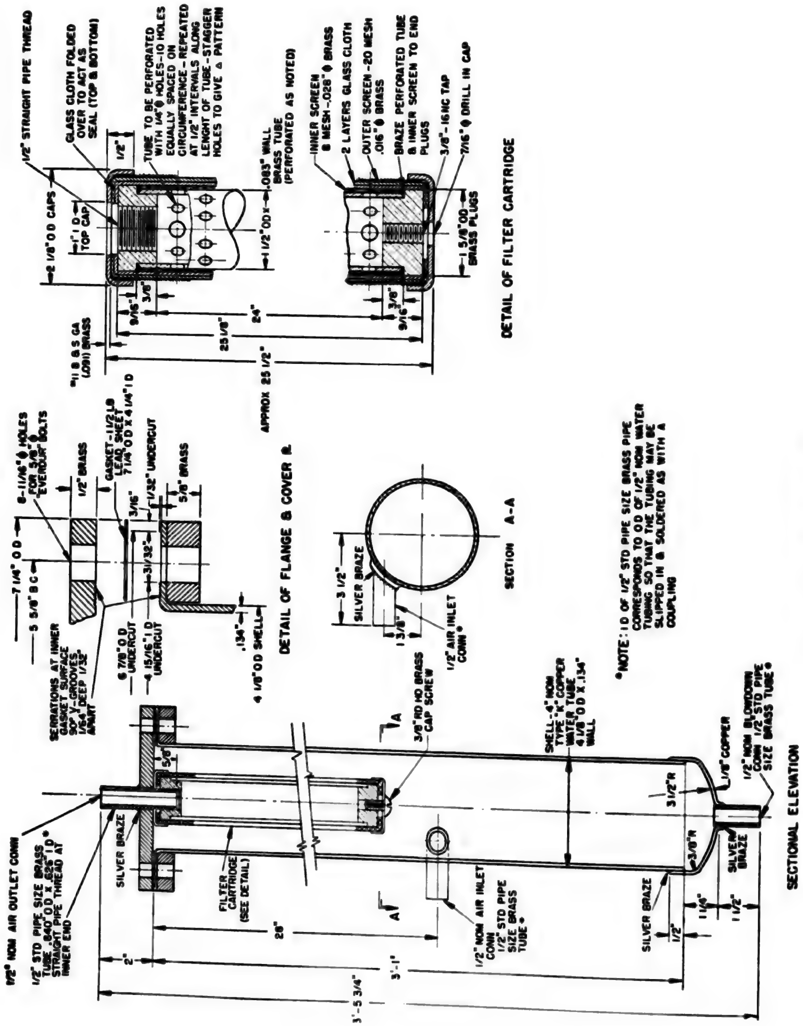


Figure 1. Carbon dioxide filter.

be removed without warming by closing off the filter from the line and quickly venting it to the atmosphere. Considerable flashing results from the depressurizing of the saturated liquid, and the flashing of liquid within and beyond the filter cake apparently disintegrates the cake and back-washes the filter element effectively. Repetition of this operation at regular intervals was almost always successful in keeping a filter running indefinitely without warming.

The detailed construction of a typical CO_2 filter is shown in Figure 1.[5]

10.3 VALVES

In general, commercial valves constructed of proper materials were suitable in the oxygen plants. For the periodic reversing of the exchangers in the low-pressure plants pneumatic quick-operating valves, either of the piston type or of the globe type, were used successfully at the warm end of the exchanger, and at the cold end commercial check valves were found entirely suitable.[5] Both manual-operated and diaphragm-operated control and shutoff valves were used successfully on cold lines in the plants. In order to minimize the refrigeration loss resulting from the direct metal connection between the external air and the cold line, the valve stems and bonnets were always extended to an appropriate length with metals of reasonably low thermal conductivity, such as German silver, stainless steel, or various copper alloys. Valve-stem stuffing boxes always were placed outside the insulation casing for reasons of accessibility and to keep the packing material as warm as possible. Pure white asbestos and paraffined white asbestos were the packing materials most frequently used.

10.4 TEMPERATURE MEASUREMENT

Copper-constantan thermocouples were generally used for the measurement of low temperatures. These thermocouples were used in the conventional fashion and conventional accuracy was obtained. Calibration of the couples at low temperatures could be made without undue difficulty at the vaporization temperature of commercial solid CO_2 and at the boiling point of pure oxygen. The thermocouples were generally used with indicating or recording potentiometers.

For more simple reading of temperature, a combination vapor-pressure and gas-pressure dial thermometer using oxygen or nitrogen was developed and placed on a production basis through co-operation with a manufacturer.[8,9] Later, dial thermometers of various types were purchased from other manufacturers. The usual accuracy and dependability of pressure-actuated dial thermometers was observed.

10.5 ANALYTICAL METHODS

In the development of oxygen plants several special analytical problems arose. The principal problems were as follows.

1. The determination of percentage of oxygen in gas mixtures, especially the analysis for purity in oxygen products.
2. The determination of CO_2 content in air in the range from 400 ppm down to 10 ppm or less.
3. The determination of hydrocarbons, especially acetylene, in air in the range from 5 ppm down to 0.1 ppm or less.

10.5.1 Oxygen Analysis

Analysis for oxygen in gases was carried out with the conventional Orsat method. For the accurate measurement for oxygen purities in the range from 97 to 100%, a measuring burette with a suitably extended scale in this range was employed. The oxygen absorbent used was copper metal washed with a solution consisting of one part of aqua ammonia and one part water, saturated with ammonium chloride. This mixture can also be used as the confining liquid in the measuring burette in analyzing high purity oxygen, and an especially convenient apparatus employing these principles is commercially available. A description and appraisal of these methods has been given.[4]

For the continuous indication and recording of oxygen partial pressure, the novel Pauling meter was developed. (See Chapter 14.)

10.5.2 Analysis of CO_2 in Air

The accurate determination of CO_2 in air in the range from the normal concentration in atmospheric air (about 340 ppm) down to the lowest measurable concentrations was of great importance in the engineering evaluation of various possible schemes of removing the CO_2 from the compressed air fed to oxygen separating plants. Two analytical methods were used for routine tests and a third method was developed as the absolute standard used for calibration of the other two.

The absolute standard adopted[8] was a titrimetric

method in which the CO_2 is absorbed in standard dilute barium hydroxide and the excess alkali is back-titrated with dilute hydrochloric acid. Repeated samples of the air to be tested are drawn into a sample bottle containing the measured standard alkali, each successive sample being removed by evacuation after absorption of the CO_2. The alkali is titrated in place in the sample bottle. This method avoids the errors introduced by exposure of the alkali to laboratory air. When the CO_2 concentration is very low an unduly large total gas sample must be taken. In this case it is convenient to condense out the CO_2 on the surfaces of a coil immersed in liquid air and then to evaporate the CO_2 into a small volume of air by warming the coil.

One of the methods used for routine determinations is a colorimetric method.[1] This method depends upon the reduction by CO_2 of the color intensity of the solution of the sodium salt of phenolphthalein. The procedure consists of the agitation of a measured volume of air with a definite volume of the indicator solution, followed by a measurement of the change in monochromatic light transmission of the solution. Great sensitivity can be obtained by suitable choice of the concentrations of alkali and phenolphthalein, and of the ratio of gas sample volume to reagent volume. The method is capable of producing satisfactory precision only if considerable care is taken both in sampling and in carrying out the analysis.

The second routine method was the use of the Pfund gas analyzer, which was developed under Division 17, NDRC. This instrument utilizes the infrared absorption characteristics of CO_2 and has proved to be completely satisfactory for the continuous analysis of gas samples. The meter is very sensitive, gives rapid readings, and, except for some uncertainty at CO_2 concentrations of 15 ppm or less, is capable of considerable accuracy.[8]

10.5.3

Low Concentrations of Hydrocarbons in Air

The need for a method of analyzing for very low concentrations of hydrocarbons in air arose from the fact that light hydrocarbons, especially acetylene, present in atmospheric air tend to accumulate in the liquid air distillation apparatus and create serious explosion hazards. In order to develop methods for removing these hydrocarbons from the air feed to oxygen separation plants, a suitable analytical method was required to determine the extent of concentration.

The procedure adopted for acetylene is a colorimetric method depending upon the formation of cuprous acetylide, which is red in color, in the reaction between a cuprous salt and acetylene.[7] A measured gas sample is reacted with measured quantities of standard reagents and the monochromatic light transmission of the resulting solution is measured. The method is standardized using known mixtures of acetylene prepared by dilution.

The method used for other hydrocarbons involves condensing the air sample in a trap cooled with liquid air boiling under reduced pressure, removing the atmospheric gases by evacuation at normal liquid air temperatures, and allowing the remaining condensables to warm to room temperature and measuring the pressure remaining in the system.[7] This method is of value only if certain assumptions can be made as to the identity of the condensable material. The method can be extended by employing it to concentrate the hydrocarbons, and then analyzing the hydrocarbons by conventional methods of gas analysis.

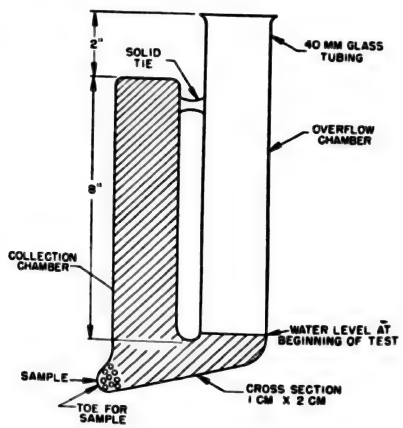


FIGURE 2. Soda lime depletion apparatus.

10.5.4

Field Method for Determining Depletion of Soda Lime

An apparatus was developed for use in the field to test the degree of depletion of soda lime used as an absorbent for CO_2 in rebreather apparatus. The specifications for the apparatus required that it be easily portable, very simple to use, as rugged as possible, and capable of accuracy within at least 20%. It was also desirable that the apparatus be suitable for measuring the depletion of Baralyme, a commercial preparation used as an alternative for soda lime.

The simple apparatus shown in Figure 2 was developed.[8] A soda lime or Baralyme sample from scoops of standard size is placed in the water-filled apparatus, and a fixed quantity of concentrated hydrochloric acid is added. The amount of CO_2 evolved is an index of depletion and is read directly on the calibrated collection chamber. Certain corrections for water temperature are made.

Chapter 11

OXYGEN GENERATION FROM REGENERATIVE CHEMICALS

By *T. A. Geissman*[a]

11.1 INTRODUCTION

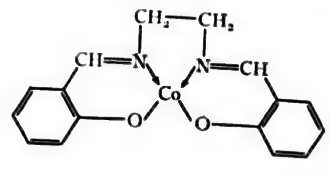
11.1.1 Salcomine and Related Materials

REGENERATIVE CHEMICALS for oxygen production gave promise of certain advantages for generation at advanced bases. Certain co-ordination complexes are able to carry oxygen reversibly and operate over convenient temperature and pressure ranges. The parent and first-known compound[40] of this type is salicylaldehyde ethylenediamine cobalt, since called "Salcomine." It is noteworthy that of the hundreds of compounds prepared and tested in the search for a substance which would carry more oxygen than Salcomine and possess a greater rate of reaction and stability, none of the very few active compounds discovered possesses a structure differing from Salcomine in a fundamental way, all of them being substitution products of the parent and most of them being 3-substituted. Indeed, from the practical standpoint, taking into account cost and availability, Salcomine itself must still be considered the most suitable compound for widespread application, although some of its substitution products have properties which make them peculiarly adaptable for certain special uses.

11.2 CHEMISTRY OF SALCOMINE AND RELATED COMPOUNDS

11.2.1 General

The property of forming coordination complexes with metallic ions is common to a large variety of organic compounds. The ability of such complexes to combine with molecular oxygen and to release it without the occurrence of other changes is found in only a very few substances. Among these are the important metal-porphyrin-protein complexes, such as hemoglobin and hemocyanin, in which the reversible oxygenation serves as a means of oxygen transport within the living organism. The only other large class of substances showing this ability, along with sufficient stability to give them practical importance, are a group of cobaltous complexes related to and exemplified by salicylaldehyde ethylenediamine cobalt, or Salcomine (I).



I

The characteristic grouping in salicylaldehyde which is responsible for its ability to form chelated metallic compounds is the *ortho*-hydroxy aldehyde grouping (II), which can form complexes such as III in which M = metal.

II III

Structure II may be generalized to include those compounds which are not simple *o*-hydroxy aldehydes, like IV, but which form metallic complexes such as V.

IV V

In this general case, Y may be not only oxygen but also other elements or groups such as the imine group (as in primary or secondary amino groups, where YH is NH_2 or NHR) or sulfur (where YH is the sulfhydryl group). Substance X may be the oxygen atom of an aldehyde or ketone carbonyl group (as in II), the nitrogen of a Schiff's base ($-CR=X$ is $-CR=N-$, as in I), or the nitrogen atom of a heterocyclic nucleus. Many other modifications of the structure IV are possible, including a number in which the coordinating group $-CR=X$ and $-YH$ are not attached to an aromatic nucleus. Among such compounds are amino acids, keto acids, thio acids, enolizable β-diketones, and imino derivatives of some of these.

[a] Professor of Chemistry at University of California at Los Angeles. From August 1943 until October 1945, Chemical Director of the Central Engineering Laboratory, University of Pennsylvania, Contract OEMsr-934.

11.3 ACTIVE SALCOMINE ANALOGUES

With the object of producing a substance of greater speed, capacity, and life than Salcomine, extensive studies were made.

1. In order to learn what effect variations in the structure of the amine or polyamine might have upon capacity, rate, and life of the chelates, a number of cobalt complexes were made using amines other than ethylenediamine, combined both with salicylaldehyde itself and with substituted salicylaldehydes. In Table 1 are listed the compounds prepared using salicylaldehyde itself, various amines, and cobalt. In Table 2 are listed compounds containing substituents in the salicylaldehyde nucleus, amines other than ethylenediamine, and cobalt.

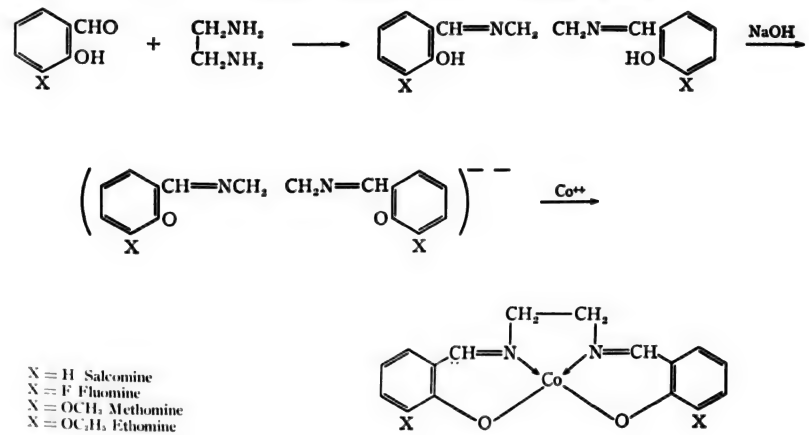
2. The use of a variety of metals other than cobalt was studied with a number of organic compounds (see Table 3). In most cases the desired complexes were obtained readily, but in no case did a complex containing a metal other than cobalt have promising oxygen-carrying activity. In those few cases where oxygen uptake occurred, the result was the nonreversible (under conditions of operation) oxidation of the metal ion to a higher state. The compounds are listed in Table 4.

3. The most important remaining direction in which improvement was sought lay in the use of substituted salicylaldehydes in place of salicylaldehyde itself. The compounds tested are listed in Table 5.

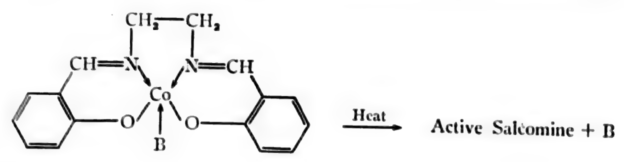
It will be seen that, of more than 200 substances examined, little or no oxygen-carrying activity is possessed by chelate compounds in which the fundamental salicylaldehyde structure is varied, or in which diamines other than ethylenediamine are used, or in which the metal is other than cobalt. Certain Salcomine derivatives prepared from substituted salicylaldehydes were found to be active, and of these several 3-substituted compounds are superior to Salcomine in rate of oxygenation. With one exception (3-fluoro-), however, they are inferior in stability and in all cases have a lower oxygen capacity. In Table 6 are tabulated those chelates which compare favorably with Salcomine.

11.4 PREPARATION

The preparation of Salcomine and similar cobalt complexes is carried out by the sequence of reactions shown in the following equations:



X = H Salcomine
X = F Fluomine
X = OCH_3 Methomine
X = OC_2H_5 Ethomine



Where B = H_2O, C_5H_5N, $C_5H_{11}N$

The important variables which affect the yield, capacity, and oxygenation rate of the final chelate are (1) the pH of the reaction mixture during the addition of the cobalt salt, (2) the volume of solution used, (3) the purity of the reagents used, (4) the presence or absence in the reaction mixture of such bases as pyridine, piperidine, or water (see below), and (5) the method of drying and activation used.[34]

When prepared in aqueous or aqueous-alcoholic solution, the chelates precipitate as crystalline hydrates. In the presence of such stronger bases as pyridine and piperidine, complexes are obtained which contain one mole of the base per mole of chelate. In general, more uniformly active products can be obtained through the pyridinates or piperidinates, but the superiority of these over those prepared by way of the hydrates is usually not great enough to counterbalance the added expense and inconvenience of using the nitrogen bases.

In any case, the water, pyridine, or piperidine is removed in the drying or activation process or in both. (See formula above.)

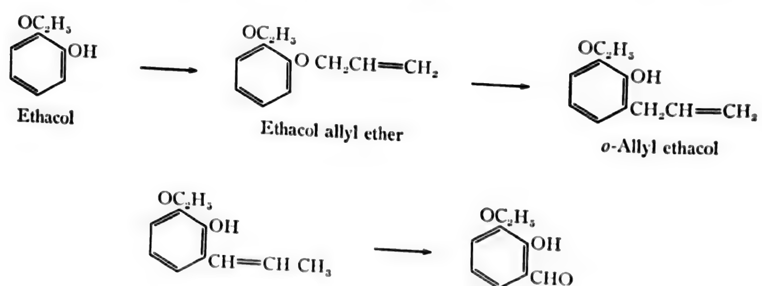
Satisfactory methods for the preparation on a large scale of uniform batches of active chelates were developed by the Rumford Chemical Works.[34,52]

The chelates as usually prepared have capacities ranging from 85 to 95% of the theoretical. The differences are often due to impurities in the raw materials used. With carefully purified materials, it has been shown in small-scale preparations that products having capacities of 95 to 99% of the theoretical can be obtained.

11.4.1 Intermediates[53,54,55]

The greatest drawbacks to the adoption of Ethomine and Fluomine for large-scale use is the inaccessibility and high cost of preparation of 3-ethoxy- and 3-fluorosalicylaldehyde. Salicylaldehyde itself is obtainable in the market in commercial quantities, but the ethoxy and fluoro compounds are not at present available, although considerable study has been devoted to the problem of preparing these aldehydes economically and in quantity.

3-Ethoxysalicylaldehyde (o-ethavan) has been available in small amounts as a by-product in the production of 3-ethoxy-4-hydroxybenzaldehyde (ethavan) by the Monsanto Chemical Co. This company has studied the problem of producing o-ethavan, and has recommended the method shown in the following equations:



Ethacol → Ethacol allyl ether → o-Allyl ethacol

o-Propenyl ethacol → o-Ethavan

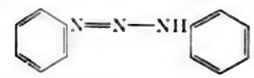
Table 1. Cobalt salicylaldehyde imines other than Salcomine.

No.	Amine	Activity	Remarks	Ref
1	Tetramethylethylenediamine $[(CH_3)_2CNH_2]_2$	Inactive		2
2	Methylenediamine $CH_2(NH_2)_2$	Inactive	Yellow complex	2
3	Pentaerythritylamine $C(CH_2NH_2)_4$	Inactive	Yellow complex	3
4	1,2-Diaminopropanol-3 $HOCH_2CH(NH_2)-CH_2NH_2$	Inactive Active 1% at 1 atm O_2; 3.42% (pressure)	Yellow-brown complex	3 6
5	Triethylenetetriamine $(NH_2CH_2CH_2NH-CH_2-)_2$	Inactive	Complex not crystalline	3
6	Tetraethylenepentamine $NH(CH_2CH_2NH-CH_2CH_2NH_2)_2$	Inactive	Complex not crystalline	3
7	dl-Propylenediamine dl-$CH_3CH(NH_2)-CH_2NH_2$	Inactive	Schiff's base not crystalline	1
8	l-Propylenediamine l-$CH_3CH(NH_2)-CH_2NH_2$	Active 4.0% Inactive		5 1
9	Sym-Dimethylethylenediamine $(CH_3CHNH_2)_2$	Inactive	Complex red, crystalline	1
10	Trimethylenediamine $(CH_2)_3(NH_2)_2$	Inactive		1 10
11	Hexamethylenediamine $(CH_2)_6(NH_2)_2$	Inactive	Complex crystalline	1
12	Nonamethylenediamine $(CH_2)_9(NH_2)_2$	Inactive	Complex tarry	1
13	Decamethylenediamine $(CH_2)_{10}(NH_2)_2$	Inactive	Complex tarry	1
14	Isopropylamine $(CH_3)_2CH-NH_2$	Inactive		1
15	o-Phenylenediamine o-$C_6H_4(NH_2)_2$	Inactive		1, 5 or 10
16	Benzidine p,p'-$NH_2-C_6H_4-C_6H_4-NH_2$	Inactive		1
17	Ammonia NH_3	Inactive		5
18	Hydrazine $NH_2 \cdot NH_2$	Inactive		5
19	o-Aminophenol o-$C_6H_4(OH)(NH_2)$	Inactive		5
20	Diethylenetriamine $NH(CH_2CH_2NH_2)_2$	Active (slow)	Chelate yellow powder	5
21	None	Inactive		5
22	Bis-trimethylenetriamine $NH(CH_2CH_2CH_2NH_2)_2$ called "prtn"	Active	11.9% in 8 days at 85 psi O_2; 1.5 hr at 100 C removed all but 3.4% of this O_2; not reversible	6
23	cis-1,2-Diaminocyclohexane	Inactive		8
24	trans-1,2-Diaminocyclohexane	Inactive		8
	Diamino dipropyl ether $O(CH_2CH_2CH_2NH_2)_2$	...	No definite complex isolated	9
26	1,3-Diaminopropanol-2 $(NH_2CH_2)_2CHOH$	Inactive		9
	2,6-Diaminopyridine	...	Only cobalt salicylaldehyde isolated	9
	2-Methylamino-1,3-diaminopropane $CH_3NH-CH(CH_2NH_2)_2$	Inactive		9
	trans-1,2-Diaminocyclopentane	Inactive		10
	Ethanolamine NH_2CH_2OH	Inactive		11
	Diaminoacetone	Some preparations show activity		12
	Tris-aminomethylmethane $CH(CH_2NH_2)_3$	Inactive		12

TABLE 2. Cobalt complexes prepared from substituted salicylaldehydes and amines and polyamines other than Ethylenediamine.

No.	Substituted salicylaldehyde	Amine	Activity and remarks	Ref
1	3-nitro	1,2-diaminopropanol-3 $HO-CH_2-CH(NH_2)-CH_2(NH_2)$	Yellow-brown inactive	3
2	5-nitro	1,2-diaminopropanol-3	Inactive	3
3	3-nitro	*bis*-diethylenetriamine $NH(CH_2CH_2NH_2)_2$	Inactive	3
4	3-nitro	triethylenetetriamine $NH(CH_2CH_2NH_2)-CH_2-CH_2-NH(CH_2CH_2NH_2)$	Oily, inactive	3
5	5-nitro	triethylenetetriamine	Oily, inactive	3
6	3-nitro	tetraethylenepentamine $NH(CH_2CH_2NH_2CH_2CH_2NH_2)_2$	Red oil, inactive	3
7	5-nitro	tetraethylenepentamine	Red oil, inactive	3
8	3-formyl-4-hydroxy	None	Yellow. Active to water	5
9	3-methyl	*bis*-trimethylenetriamine [prtn] $NH(CH_2CH_2CH_2NH_2)_2$	Active. Not completely reversible	6
		prtn	Some inactive. Some preparations 6.5%.	8
		prtn	6–7% at 150 psi O_2 at room temp, 7.6% at 100 psi O_2 at 0°C; successive preparations	9
10	5-methyl	prtn	6.9%. Only partially reversible	6
11	3-methoxy	prtn	5.7%. Only partially reversible	6
12	3-nitro	prtn	3.47% (175 psi O_2). Reversible	6
13	3-chloro		Inactive, by treating active form with pyridine	7
14	5-nitro	prtn	4.7% high press. Reversible	6
15	5-chloro	prtn	1.5% weakly active	6
16	5-hydroxy	prtn	< 1% weakly active	6
17	4-hydroxy	prtn	Inactive	6
18	3-ethyl-4-hydroxy	prtn	Inactive	6
19	3-ethyl-4-methoxy	prtn	1.25% weakly active	6
20	3-allyl	prtn	5.6% in 2 hr at 175 psi O_2. Reversible	6
21	4-methoxy	prtn	Inactive	7
22	5-amino	prtn	Some activity. Oxidizes while wet	7
23	3-ethyl-4-hydroxy-5-formyl	prtn	Black, inactive	8
		prtn	Not reversible. 3.6% at 1 atm, 4.8% at 200 psi O_2	8
24	6-chloro			
25	4-nitro	prtn	Br-yellow hydrate, sl. activity up to 2.5%	8
26	3-isopropyl-6-methyl	prtn	Sl. active	8
27	3-methyl-6-isopropyl	prtn	4.65% at 200 psi O_2 deteriorates rapidly	8
28	3-chloro-5-tert. butyl	prtn	6.3% at 175 psi O_2. Not reversible	8
29	3-*n* propyl	prtn	Sl. active	8
30	3-phenyl	prtn	Inactive	8
31	5-tert. butyl	prtn	Inactive	8
32	4-ethoxy	prtn	No complex isolated	9
33	4-hydroxy-6-methyl	prtn	Inactive	9
		prtn	7.3% at 225 psi O_2 in 12 hr; then 4.5% at 1 atm difficult to prepare, active	9
34	4,6-dimethyl			
35	3-methyl-6-chloro	prtn	Br-y, sl. active	9
36	5-carbomethoxy-6-hydroxy	prtn	3% at 150 psi O_2	10
37	3-ethyl	prtn	Inactive	10
		prtn	3.6% at 200 psi O_2, 2.7% at 1 atm.	11
38	3-fluoro	prtn	Very fast deterioration	
39	4-methoxy-6-methyl	prtn	4–5% but requires press.	12
			Some activity	9

TABLE 3. Chelates containing metal[illegible]

No.	[illegible]onyl compound	Amine	Metal	[illegible]	Ref
1	Salicylaldehyde	en*	FeII	Inactive	1
2	5-[illegible]mosalicylaldehyde	en*	Mn	Inact., oxid. to FeIII	5
3	Pyruvic acid	en*	FeII	Inactive	1
4	Pyruvic acid	*dl*-1,2-diaminopropane	FeII	Inactive, ferrous state estab. by test	1
5	Pyruvic acid	*o*-phenylenediamine	FeII	Inactive. FeII estab. by test	1
6	Salicylaldehyde	*o*-phenylenediamine	FeII	Inactive	1
				Inactive	1
7	Vortmann's sulfate	...	...	None	5
8	Phthalocyanine	...	FeII	None	5
9	Quinaldinic acid	...	FeII	Violet. None	5
10	Salicylaldehyde	Diethylenetriamine $NH(CH_2CH_2NH_2)_2$	FeII	None	5
				None	5
11	Salicylaldehyde	*o*-aminophenol	FeII	Oxidized to FeIII. None	5
12	2-Hydroxybenzamide	...	FeII	Oxidized to FeIII. None	5
13	2-Aminobenzaldehyde	en*	FeII	Oxidized to FeIII. Chelate not isolated	5
14	Violuric acid	...	FeII	Inactive	5
15	Picolinic acid	...	FeII	Hard to isolate. No conclusions	5
16	Salicylaldehyde	en*	Mn	Active, oxidized	5
17	Salicylaldehyde	Diethylenetriamine	Mn	Yellow. None	5
18	Salicylaldehyde	...	Cu	None	5
19	Salicylaldehyde	en*	Cu	None	5
20	Salicylaldehyde	Diethylenetriamine	Cu	None	5
21	Diazoaminobenzene 	...	Ni	None	5
22	Salicylaldehyde	...	Ni	None	5
23	Salicylaldehyde	en	Ni	None	5
24	Salicylaldehyde	en	Vanadyl	None	5
25	Salicylaldehyde	prtn	FeII	No complex isolated	9
26	Salicylaldehyde	Trimethylenediamine	Cu	Inactive	11

* Ethylenediamine [en] $(NH_2CH_2CH_2NH_2)$

The yields to be expected in this process are as follows: *o*-allyl ethacol on ethacol consumed, 81% of theory; *trans-o*-propenyl ethacol on *o*-allyl ethacol, 70% of theory; *o*-ethavan on *trans-o*-propenyl ethacol, 7[illegible]–73% of theory; overall yield, 40–41% of theory.

3-Fluorosalicylaldehyde has been prepared by the reactions shown in the following equations:

The maximum yields obtained in these reactions are: *o*-anisidine ⟶ diazonium borofluoride, 90%; diazonium borofluoride ⟶ *o*-fluoroanisole, 65%; *o*-fluoro-anisole ⟶ *o*-fluorophenol, 86%; *o*-fluorophenol ⟶ 3-fluorosalicylic acid, 55%; 3-fluorosalicylic acid ⟶ 3-fluorosalicylaldehyde, 55%; overall yield, 15%.

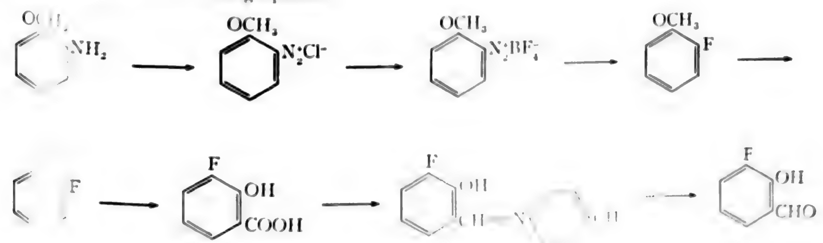


TABLE 4. Cobalt complexes prepared from carbonyl compounds other than salicylaldehydes or substituted salicylaldehydes and amines and polyamines of all types.

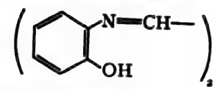
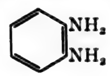
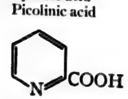
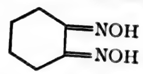
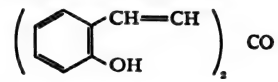
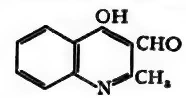
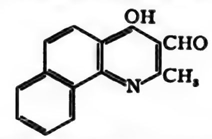
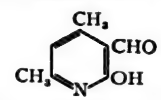
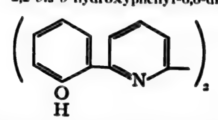
No.	Carbonyl compound	Amine	Activity and remarks	Ref
1	2-Hydroxyacetophenone	Ethylenediamine [en] $NH_2CH_2CH_2NH_2$	4.0%, slow, and only under 200 psi	1
			Red, cryst., some activity	5
			Ca. 2%, difficult to prepare active sample	7
			4.53% at 100 psi O_2	13
2	2,4-dihydroxyacetophenone	en	Slight	1
			Red. None	5
3	2-hydroxy-propiophenone	en	Could not form chelate	4
			Cryst. inactive	5
4	2-hydroxy-5-methyl-acetophenone	en	Red. 1.0% (?). 200 psi O_2	4
5	2-hydroxy-4-methyl-acetophenone	en	Brown. Inactive	4
6	2-hydroxy-3-nitro-acetophenone	en	Red. Inactive. Chelate not analyzed	4
7	Ethylene *bis*-thioglycolic acid $(-CH_2S-CH_2COOH)_2$	...	Violet, cryst., inactive	4
8	Glyoxal *bis*-*o*-hydroxyanil 	...	Inactive	3
9	Formyl camphor $C_{11}H_{16}O_2$	en	Inactive	2
10	Formyl camphor	*o*-phenylenediamine 	Inactive	2
11	Pyruvic acid $CH_3COCOOH$	en	Inactive	1
12	Pyruvic acid	*dl*-1,2-diaminopropane	Inactive	1
13	Pyruvic acid	*o*-phenylenediamine	Inactive	1
14	Picolinic acid 	None	Orange. None	5
15	2-aminobenzaldehyde	en	Red, cryst. None	5
16	8-hydroxyquinoline	None	Yellow. None	5
17	2-hydroxybenzamide	None	Yellow. None	5
18	2-aminophenol	...	Brown-pink. None	5
19	Acetylacetone $CH_3COCH_2COCH_3$	None	Cryst. None	5
20	Ethyl acetoacetate CH_3COCH_2COOEt	None	Cryst. None	5
21	Methyl acetoacetate $CH_3COCH_2COOCH_3$	None	Cryst. None	5
22	Acetylacetone	en	Cryst., active, eventually oxidizes	5
23	2-hydroxyacetophenone	prtn	Inactive	6
24	Naphthazarin	...	Active 3.22%. Deteriorates rapidly	7
25	1,2-cyclohexanedione dioxime 	...	Sl. activity	8
			Sl. activity	8
26	1,2-cyclopentane-dione	en	... Schiff's base decomposes	9
27	2-5-dihydroxy acetophenone	en	... Could not obtain chelate	12

TABLE 4 (*Continued*)

No.	Carbonyl compound	Amine	Activity and remarks	Ref
28	Dithio oxamide $NH_2CSCSNH_2$	...	Complex decomposes	12
29	*bis*-(*o*-hydroxybenzal) acetone 	...	Inactive	12
30	2-orthohydroxyphenyl quinoline	...	Inactive	13
31	1-orthohydroxyphenyl isoquinoline	...	Inactive	13
32	3-formyl-4-hydroxy-6-methyl-quinaldine	en	o-r. cryst. inactive	13
33	3-formyl-4-hydroxy-quinaldine 	en	Yellow, inactive	13
34	7,8-benzo-3-formyl-4-hydroxy-quinaldine 	en	Yellow, inactive	13
35	2-hydroxy-3-formyl-4,6-dimethyl-pyridine 	en	Complex not obtained	13
36	2-hydroxyacetophenone	1,2-diaminopropane	Inactive	13
37	2-hydroxyacetophenone	Trimethylenediamine $(CH_2)_3(NH_2)_2$	Inactive	13
38	2-hydroxy-3-ethoxy-acetophenone	en	... 1% (pressure)	13
39	2-hydroxy-3-methoxyacetophenone	en	Active, requires high pressure O_2	13
40	2,2-*bis*-*o*-hydroxyphenyl-6,6-dipyridine 	...	Red, cryst., inactive	13

11.5 OXYGENATION-DEOXYGENATION REACTION

A thorough study has been made of the reaction between oxygen and cobalt chelates of the Salcomine type. The aspects of the reaction examined in detail are as follows.

1. The heat of the reaction

$$2\ \text{chelate} + O_2 \rightleftharpoons \text{chelate} - O_2 - \text{chelate}$$

2. The equilibrium between oxygen and the chelate.
3. The rate of the oxygenation reaction, with respect to the oxygen pressure and the temperature.
4. The crystal structures of the various forms (active, inactive, oxygenated, deteriorated) of several chelates, determined by means of X-ray studies.
5. The magnetic properties of the oxygenated and oxygen-free chelates.

TABLE 5. Cobalt salicylaldehyde ethylenediamines containing substituents in the salicylaldehyde nucleus.

No.	Substituted salicylaldehyde	Activity	Remarks	Ref
1	4-hydroxy	Inactive	Structure of chelate doubtful	3
		4%	Stable, red cryst.	5
2	4-methoxy	3.0%	Active if activated at 120–130 C	3
			Inactive after heating at 160 C	
		4.34%	Requires high press. Reversible	
3	5-hydroxy	Turns black in air, but inactive after deoxygenation		6
4	3-chloro	5.2% (pressure)	Not reversible	8
		1.9%	Slow	3
5	5-ethyl	Inactive	Forms pyridine peroxide	6
6	3,6-dimethyl	4.2%	Comparable to Sal.	3
7	4,6-dimethyl	Inactive		3
8	5-methyl	Inactive		3
		2.7% on preparation in 50% alc.	Preparations from Na salt of Schiff's base inactive	1
9	4-methyl } 6-methyl }	1.56%; inactive in air	Mixture of aldehydes used	1
	4-methyl	Inactive		
10	3-methyl	Inactive		8
		Inactive		1
11	3-methoxy	Active, fast, reversible "Methomine"		6
		Active, very rapid to theoretical capacity		1
12	3-methoxy-5-nitro	Inactive		8
13	5-bromo	Inactive		—
14	3-nitro	3.83%		1
15	5-nitro	Inactive	Fast, sensitive to water	1
		1.5%		1
16	2-hydroxy-1-naphthaldehyde	Inactive	Red cryst., stable	5
17	3-carboxy	Inactive		1
		1%	Chelate tarry; structure doubtful	4
18	3,5-dibromo	Inactive	Red; cryst.	12
19	5-chloro-6-methyl } 6-chloro-5-methyl }	Inactive		4
20	3-ethoxy		Mixture of aldehydes used	4
21	3-propoxy	Active, fast, reversible	Ethomine	2
22	5-ethoxy	3.5%, fast	Hygroscopic	2
23	3-bromo	Inactive		2
		Inactive	Yellow to red-brown. No color change on drying at high temp.	2
24	3-isopropyl-6-methyl	Inactive		
25	3,5-dimethyl	Inactive		4
26	3,5-di-*tert*-amyl	Inactive		8
27	3-*tert*-amyl	....		4
28	3-methyl-5-*tert*-amyl	Inactive	Poor yields; abandoned	4
29	3-chloro-5-*tert* butyl	Inactive		4
		Inactive		4
30	3-bromo-5-*tert* butyl	Slightly active		4
31	3-isopropyl-5-chloro-6-methyl	Inactive		8
32	3-*n*-butoxy	Inactive		4
33	5,6-dimethyl	3.3%, very fast		4
	4,5-dimethyl	Inactive	Cryst.	4
34	5-*tert* butyl-6-methyl }		Mixture of aldehydes used	4
	4-methyl-5-*tert* butyl }	Inactive		
35	3-formyl-4-hydroxy		Mixture of aldehydes used	4
36	5-chloro	6%, slow		
37	4-nitro	Inactive	Constitution of chelate unknown	5
		1.5%	Brown, cryst.	5
38	5-methoxy	4.2%	Red, cryst. stable	5
39	3-allyl	Inactive	Reversible	8
40	3-ethyl-4-methoxy	Inactive (?)		6
41	3-ethyl, 4-hydroxy, 5-formyl	Inactive	Some preparations show some activity	7
42	5-amino	2% at 1 atm O_2 5.74% under press.		[illegible]
43	6-chloro	1% at 1 atm 2% (pressure)	Deteriorates; very insoluble	[illegible]
		Inactive	Black	[illegible]

TABLE 5 (*Continued*)

No.	Substituted salicylaldehyde	Activity	Remarks	Ref
44	3-methyl-6-isopropyl	Inactive		8
45	3-phenyl	Inactive		8
46	3-*n*-propyl	Inactive		8
47	5-carbomethoxy-6-hydroxy	Inactive		8
48	3-fluoro	Active, very fast reversible	Fluomine	10
49	5-propionic acid	Inactive		12
50	6-methoxy	Inactive		12
51	4-hydroxy-6-ethyl	Inactive		13
52	6-methyl	1.5% (pressure)		13
53	3-ethyl	Inactive	Cryst.	12
54	5-fluoro	Active (theor.) very slow	Red-brown	13

TABLE 6. Active Salcomine derivatives: Co-X-Sal-en*.

Chelate	Oxygen capacity	Remarks
Co-Sal-en	Theoretical capacity†	Salcomine‡
Co-3-OEt Sal-en	Theoretical capacity†	Ethomine‡
Co-3-OMe Sal-en	Theoretical capacity†	Methomine‡
Co-3-NO_2 Sal-en	3.83%	Fast, sensitive to water
Co-3-F Sal-en	Theoretical capacity†	Fluomine‡
Co-3-OPr Sal-en	3.5%	Fast, deteriorates rapidly, sensitive to H_2O
Co-3-OBu Sal-en	3.5%	Fast, deteriorates rapidly
Co-4-OH Sal-en	4%	....
Co-4-OMe Sal-en	4.34%	Requires high pressure
Co-5-Et Sal-en	4.2%	....
Co-4-NO_2 Sal-en	4.2%	....
Co-5-F Sal-en	Theoretical capacity†	Very slow

* Co-X Sal-en is an abbreviation for X-substituted-salicylaldehyde ethylenediamine cobalt.
† The theoretical capacities of 1 atom of O per molecule of chelate have been realized on carefully made laboratory preparations, although the usual materials manufactured on a semi-plant scale have capacities of 90–95% of the theoretical.
‡ The substances to which trivial names have been assigned are those which were prepared and tested on a large scale for the purpose of gathering data for engineering design of practical operating units.

6. Changes in the structure of Salcomine crystals during the course of oxygenation (determined by means of photomicrographs).

7. The mechanism of the reaction, deduced from the data obtained by the above experimental procedures.

11.5.1 Heat of Reaction

Chelates of the diamine type have a ΔH of 18–21 kcal per mole of oxygen, while the single example of the triamine (prtn) type has a lower ΔH, about 15 kcal per mole.

11.5.2 Equilibrium Vapor Pressure of Oxygenated Chelates

By raising slowly the temperature of an oxygenated sample of chelate at constant pressure and measuring the oxygen evolved at a series of temperatures, a plot of composition vs temperature can be constructed. Two typical plots obtained in this way, for Ethomine and Fluomine,[51] are shown in Figures 1 and 2.

11.5.3 Rate of Oxygenation Reaction

Typical absorption rate curves are shown in Figures 3 and 4. The data are taken by the following generalized procedure.

A sample of the deoxygenated chelate is brought to a constant temperature, and oxygen (or air) is admitted to a desired pressure. Oxygen (or air) is then admitted to the system at such a rate as to maintain the initial pressure over the compound, the rate of admission, and thus the rate of absorption, being measured by the change in volume or of pressure of a calibrated reservoir. It is seen from Figure 4 that the rate of absorption is influenced by the oxygen pressure. This is shown more clearly in Figure 5 in which the (second-order) absorption rate constant for Fluomine is plotted vs the oxygen partial pressure.

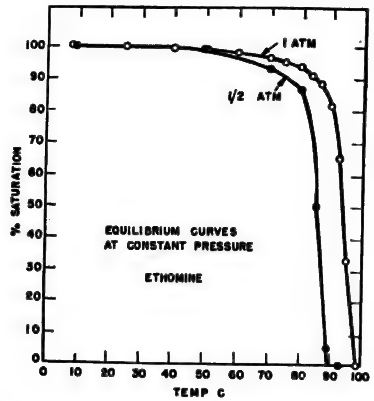


FIGURE 1. Equilibrium curves at constant pressure. Ethomine.

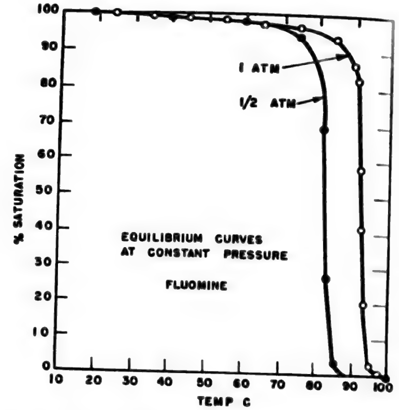


FIGURE 2. Equilibrium curves at constant pressure. Fluomine.

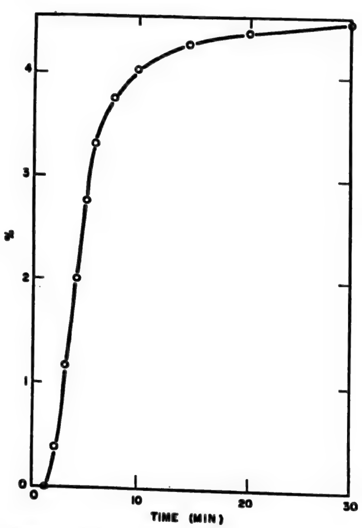


FIGURE 3. Typical absorption rate curve. Co-Sal-én at 25 C, 760 mmO_2.

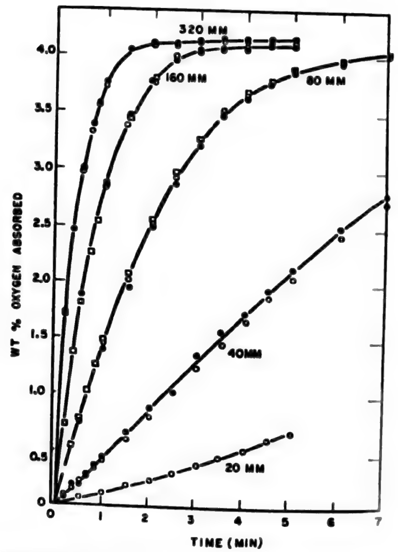


FIGURE 4. Oxygen absorption rate curve. Fluomine at 20 C.

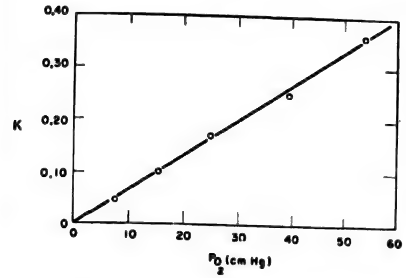


FIGURE 5. Fluomine. Second-order absorption rate. Constant temperature vs pressure ($T = -40$ C).

Since the equilibrium vapor pressure of oxygen over the oxygenated chelates increases with temperature, it follows that the rate of absorption will show a maximum at a temperature which is characteristic of the compound. Typical curves showing this effect in the case of Ethomine are given in Figure 6. In

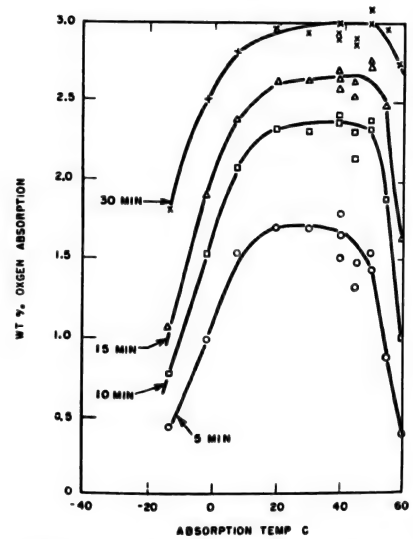


FIGURE 6. Optimum absorption temperature of Ethomine. Air pressure: atmospheric. Air rate: 3 cfh/40.7 g, ½-in. tube unit.

Table 7 are given optimum absorption temperatures for several compounds.

TABLE 7. Optimum absorption temperatures for several compounds.

Compound	Optimum absorption temperature
Salcomine	5 C
Ethomine	25 C
Fluomine	35 C

11.5.4 Crystal Structure of the Chelates[22,24,25]

Salcomine has been studied intensively by means of powder photographs.[23] The structure is relatively simple (Figure 7). It will be noted that there are holes running through the structure parallel to a_0. Possibly oxygen may pass from one cavity to another and thus be transferred by a sort of diffusion from an oxygenated molecule to an unoxygenated one. Two other active derivatives of Salcomine, namely, Fluomine and CO-*o*-hydroxyacetophenon-en, yield powder photographs strikingly similar to those from Salcomine itself. If the structures are essentially the same (coplanar layers of molecules) the chief effect of the substituents will be to expand the structure in the b_0 direction, with the result that the holes in the structure are slightly larger in the case of these 3-substituted compounds than in Salcomine.

The size of these passages through the structure is evidently not the only factor in determining the speed of oxygenation of a given chelate, since the 3-chloro-derivative of Salcomine, which would be expected to show holes larger than those in Fluomine, is inactive; and CO-*o*-hydroxyacetophenone-en, comparable in structure to Fluomine, is much slower in its rate of oxygenation.

11.5.5 Magnetic Properties of the Cobalt Chelate[10,11,19,20,24]

Measurements have been made of the magnetic susceptibilities of many forms of Salcomine and its analogues, including such modifications as solvated complexes, active and inactive forms, and oxygenated forms. The results can be summarized as follows.

1. Active diamine complexes, for example, Salcomine and Fluomine, contain *one* unpaired electron in the oxygen-free state, and are essentially diamagnetic when oxygenated to the 2/1 oxide. The paramagnetism shows a linear decrease with increasing per cent of oxygenation between these extremes.

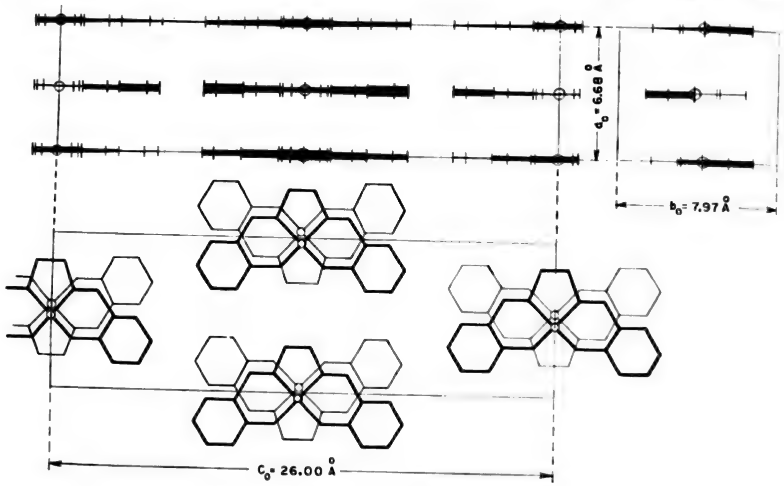


FIGURE 7. Crystal structure of Salcomine.

2. Active triamine (prtn) complexes contain *three* unpaired electrons before oxygenation, the oxygenated (1/1) form having *one* unpaired electron.

3. Some inactive forms of diamine complexes show *three* unpaired electrons per cobalt atom.

4. Solvated diamine complexes show *one* or *three* unpaired electrons. Occasionally a sample showing two unpaired electrons has been encountered, and this has been assumed to be the result of the presence of a mixture of forms.

In the case of the diamine complexes, the magnetic properties of the active forms constitute good evidence that the molecule is coplanar, the four filled coordination positions of the cobalt atom being situated at the corners of a square.

11.5.6 Changes in the Gross Structure of Salcomine Crystals during Cycling

A series of photomicrographs ($\times 125$) have been made of a single, active crystal of Salcomine, 0.29×0.03 mm, through four cycles. Cycling was produced by oxygenating the crystal under 1 atm pressure of O_2, and deoxygenating upon a hot stage on the microscope.

The following observations were made.

1. Oxygenation splits and bends the crystal.

2. Simultaneous with this rupture, there is an increase in the length and decrease of the width of the crystal. The areas remain constant.

3. On deoxygenation, the crystal tends to return to its original form.

Figure 8 shows an enlargement ($\times 2{,}000$) of a crystal which has been cycled four times. It shows the pattern of cracks developing which have not yet reached the stage of actual separation of the finer fragments. These fragments have a diameter of approximately 5×10^{-4} mm.

Since the ability of this material to hold oxygen depends upon the cooperation of two molecules arranged in a very specific lattice, it would appear that this particle size reduction may be an important factor in capacity reduction on cycling; and it may account in part for the observation that loss in oxygen capacity upon deterioration always exceeds the loss in the amount of chemically intact Salcomine in the same sample.

11.5.7 Mechanism of the Oxygenation Reaction[13,20,21,22]

The mechanism of the reaction between Salcomine et cetera, and oxygen has been studied with the aid of the experimental methods outlined in the fore-

going sections, the principal source of information being the analysis of the dependence of the rate of the reaction upon chelate composition, temperature, and oxygen pressure.

FIGURE 8. Enlargement ($\times 2{,}000$) of a crystal which has been cycled four times.

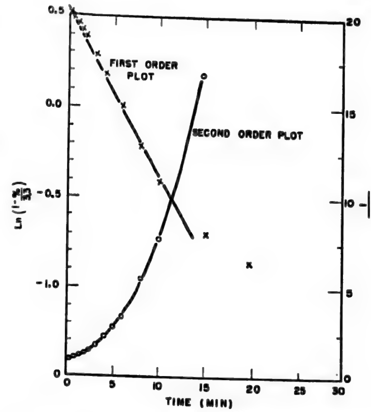


FIGURE 9. Typical plot of rate data. Ethomine (15 C) Reaction order test.[13]

For Salcomine and Ethomine, the reaction follows the first-order law. A typical plot of some rate data is shown in Figure 9, in which it is seen that the first order law is followed closely except at very low and very high degrees of oxygenation.[13] Figure 10 shows a similar plot in which it is apparent that the order of the reaction is not modified by changes in the oxygen pressure.

For Fluomine, the reaction at low oxygen pressures appears to be second order with respect to the chelate, although at high oxygen pressures there is some indication that it is first order. There is also an indication that, at an oxygen pressure at which the reaction is second order at low temperature, it may become first order at higher temperatures.

It has been established that, in the case of all of the diamine chelates, a marked induction period in the uptake of oxygen appears at high temperatures (above the optimum temperature).

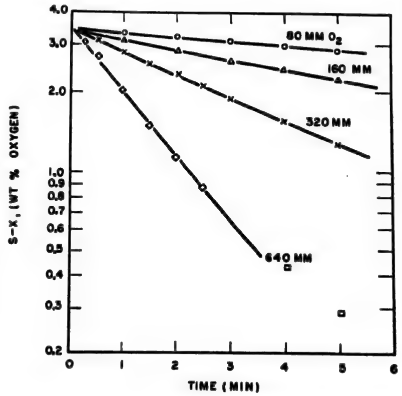


FIGURE 10. Typical plot of rate data. Ethomine (−10 C). First order test.[21]

From the practical standpoint, the existence of an induction period would limit the useful range over which the compound can be oxygenated in the course of a complete cycle of absorption and desorption. It would be desirable to carry out the deoxygenation to such an extent only as to leave the desorbed com-

pound partially oxygenated, so that upon reoxygenation the induction period would not appear. In other words, that portion of the absorption rate curve which is essentially a straight line would be used in a cycle.

11.6 ENGINEERING EVALUATION OF SALCOMINE AND ITS CONGENERS

11.6.1 General Introduction

For the design of a unit for the production of oxygen by means of Salcomine, Ethomine, or Fluomine, one of the most important factors is the heat load for which provisions must be made over a complete cycle of operation. Since during oxygenation an amount of heat is evolved equal to about 19 kcal per mole of oxygen absorbed, the temperature of the absorbent would rise sharply unless some means were provided for dissipating this heat. If this heat were not removed and the temperature of the absorbent allowed to rise, the rate of oxygenation would decrease because of the increase in back pressure of oxygen over the oxygenated chelate. This could be overcome by using an initial oxygen (or air) pressure so high that a large excess driving force would always be present, but there are reasons why this is impractical. The most satisfactory procedure is to use a suitable heat exchanger in which controlled removal of heat during oxygenation and controlled addition of heat during desorption can be accomplished.

Important information about the practical utilization of these absorbents has been gained in experiments carried out in apparatus which compares closely with large-scale equipment in heat-transfer and pressure-drop characteristics, and in which repeated cycling can be carried out, but which is constructed on a smaller scale. Most of the testing of the various chelates which were selected for intensive study was carried out in apparatus holding from about 0.1 to 35 lb of chelate and in which provision was made for automatic control of fixed cycles which could be repeated for any desired length of time.

11.7 THERMAL PROPERTIES OF SALCOMINE[30]

The important thermal properties of Salcomine, et cetera, are (1) the specific heat, (2) the thermal conductivity, and (3) the heat of reaction. The last of these has already been discussed.

The specific heat of Salcomine was determined calorimetrically, and found to be 0.24 Btu per lb per degree Fahrenheit. The specific heats of Ethomine and Fluomine have not been determined but are presumably about the same.

The thermal conductivity of Salcomine obviously depends upon its state of aggregation, whether it is in powder or granular form, and the degree of compression of the granules. Attempts have been made to increase the thermal conductivity (and heat capacity) of Salcomine by the addition of metallic powders[28] in Table 8 are given the thermal conductivity, k, in Btu per (hr) (sq ft) (°F) per ft, of various granules and pressed cakes. These data were obtained from steady state measurements at an average temperature of about 35 C.

Table 8. Thermal conductivity of various granules and pressed cakes.

Material	Thermal cond., k	Spec grav
Salcomine 10 to 20 mesh	0.0366	0.65
Salcomine cake pressed 3,640 psi	0.0990	1.10
3,640 psi plus 10% aluminum	0.105	1.23
3,640 psi plus 10% bronze	0.098	1.18

It is apparent from these data that the thermal conductivity is very low and is not appreciably increased by metallic additives. The considerable increase in weight resulting from adding metal powders, coupled with a reduced weight of chelate per pound of charge, overbalances any small advantage that might be gained by such additions.

Attention was also directed to an examination of the heat transfer properties of beds of Salcomine. Theoretical and experimental investigations have shown that the heating or cooling time of a cylindrical bed of Salcomine is proportional to the square of the radius of the cylinder. In Figure 11 are shown heating and cooling curves of cylindrically packed beds of Salcomine in ½-in. and 1-in. tubes. It is at once apparent that the use of small diameter tubes (or short conduction paths) offers a distinct advantage. The advantage, moreover, is much greater than can be shown by such data as these, since in a bed in which a long conduction path exists, the chelate near the heating surfaces must be maintained at a high temperature for an extended period in order to allow the heating of material distant from the heating surfaces, thus causing rapid and extensive deterioration in activity.

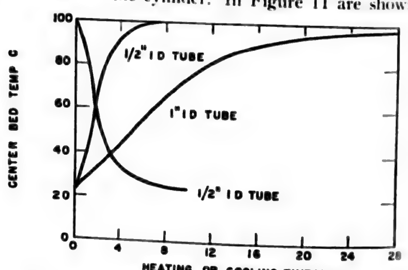


Figure 11. Heating and cooling curves of cylindrically packed beds of Salcomine.

11.8 METHODS OF OPERATION OF THE CYCLE

Since Salcomine, Ethomine, and Fluomine are best oxygenated at a low temperature under pressure, and deoxygenated at elevated temperatures under reduced pressure, the necessity for cooling and heating the considerable mass of the reactor in which the granules are packed imposes the requirement for furnishing and removing much more heat than that of the reaction alone. It would be a distinct advantage if a system could be devised whereby the chelate alone would have to be heated and cooled, or in which the heat of the reaction could be stored in the chelate itself, enough pressure being used in the latter case to give rapid oxygenation at a relatively high temperature. Systems utilizing these principles of operation have been studied experimentally, and are described in the following sections.

11.8.1 The Fluidized System

Fluidized operation consists of suspending powdered Salcomine in a fluid, either the air from which oxygen is being absorbed, or some inert fluid such as an oil, and circulating the suspension through the cooled absorption zone and the heated desorption zone. This kind of operation possesses several advantages over the stationary packed bed. The output of oxygen is continuous, thus making it unnecessary to have several units operating on staggered cycles and greatly simplifying the problem of control. The major part of the heat load is eliminated, as only the powder is heated and cooled, and the problem of heat transfer to the absorbent is simplified because of the intimate contact between the powder and the heating and cooling media.

Suspension in Air[30]

An experimental study was made of the fluidized system, in which the powder was suspended in air during absorption and in heated, recirculated oxygen during desorption.

While this system appears simple, it was found to be impractical from the standpoint of ease of operation, reliability, and portability. Estimates indicate that a unit of this type would weigh more than a stationary bed unit of the same oxygen capacity. In the light of subsequent experience it is also probable that it would be difficult to operate a fluidized cycle in such a way as to avoid rapid deterioration of the chelate.

11.8.2 Salcomine-in-Oil System[31,32,33]

The investigation of the process of oxygen production by means of a circulating suspension of Salcomine in a refined white oil was carried out on a semi-plant scale. The oil used was a highly refined hydrocarbon oil containing only saturated paraffins and saturated naphthenic constituents. The Salcomine was suspended in the oil by ball milling, the suspension containing about 25% solids.

The apparatus consisted of a stirred autoclave, in which the Salcomine suspension was treated with air at about 20 C and 150 psi. The suspension flowed from the autoclave into a separator where residual air and nitrogen was removed at 10 to 25 in. Hg vacuum through a heater into a desorbing tower, and then through a cooler from which a pump returned it to the autoclave. The rate of production of oxygen in this system was about 50 to 60 cu ft per hr.

The useful life of Salcomine under these conditions is only about 150 hr, corresponding to about 300 cycles. This is a very unsatisfactory life in comparison with that which can be realized in a properly designed packed bed unit.

11.8.3 "Circulating Solid" System[43]

In this system, for which experimental apparatus was built and tested, the absorbent such as Salcomine or methomine in powder form is circulated by means of a screw conveyor, first through a chamber in which absorption conditions prevail, and then through a second chamber in which desorption conditions prevail. The reactant may therefore be circulated cyclically, passing the powder reactant through gas-tight locks. Many of the advantages of "fluidized" operation should be possible.

11.8.4 Adiabatic and Semi-adiabatic Operation[30]

The immediate advantage of adiabatic operation is that the heat of reaction of Salcomine and oxygen is stored in the compound and becomes available for desorption. In this way the overall heat load is substantially reduced. In semi-adiabatic operation, the heat furnished by an absorbing bed is used to heat a bed undergoing desorption, the system as a whole being adiabatic.

Several disadvantages in such systems are at once apparent. In order to produce a temperature in the oxygenated bed sufficient for rapid desorption, the temperature must be allowed to rise to such a degree that considerable pressure must be applied during absorption to overcome the considerable back pressure of oxygen over the hot, oxygenated bed; or else a smaller amount of absorption must be accepted. For this reason the amount of absorbent and the reactor weight would be large. The oxygen purity would be low since pumping out inerts before desorption would reduce the yield of oxygen considerably because of the "flashing" off of oxygen from the hot bed upon release of pressure. The high temperature level during absorption and desorption would be expected to reduce the useful life of the absorbent.

Since the life of Ethomine was found to be very short under the conditions of adiabatic operation it was believed that a compound (or mixture) having a lower operating temperature would be more stable. In Table 9 is given the total production of various

Table 9. Total production of various mixed chelates.

Compound	Operating temperature	Life*
Ethomine	90 C	7
Ethomine-Salcomine 1:1	30 C	3
Methomine-Ethomine 3:1	50 C	9
Methomine-Ethomine 1:1	60 C	10

*Total production, lb O_2 per lb compound, operating at 250 psi absorption, 0.1 atm desorption, circulating fluid semi-adiabatic unit.

mixed chelates. It is apparent that there is no regular relationship between life and optimum operating temperature, and that the total productive capacity of any of the substances tested under these conditions is quite low.

It was concluded that the semi-adiabatic system would make an ideal field unit if a suitably stable compound were available. Fluomine might be such a compound but it has not been tested under these conditions.

11.8.5 Packed Beds in Heat Exchangers

The ½-in. Tube Unit[23]

The results of studies of the fluidized and adiabatic systems led to the conclusion that the most effective method of operation of Salcomine-like compounds would prove to be in a system operating as follows.

1. Absorption under superatmospheric pressure, with a cooling fluid to carry away the heat of reaction and to maintain the bed at a suitable absorption temperature.

2. Desorption under atmospheric or reduced pressure, with a heating fluid to supply the heat of reaction.

The important operating variables for this kind of operation are (1) the time of the absorption and desorption periods, (2) the temperature of the cooling water, (3) the air pressure used, (4) the temperature of the heating fluid, (5) the pressure of desorption, (6) the quality (humidity, cleanliness, et cetera) of the air used, and (7) miscellaneous factors, such as the kind of chelate, its history, pellet size, and hardness.

The ½-in. tube unit is shown in Figure 12. Air was cleaned, filtered, and dried (if desired), and the temperature of the steam used for desorption was controlled by suitable throttling. The standard test weight of absorbent used was 42.5 g, and an air rate

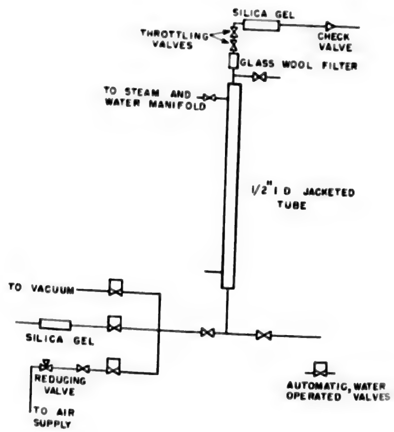


Figure 12. General piping diagram of ½-inch unit.

of 3 cfh per tube was used as standard for most of the tests. Automatic control of the cycle was provided by a timer which operated the water-actuated piston valves. In later modifications of this apparatus bellows-operated valves were adopted as most satisfactory.

The oxygen evolved upon desorption was collected over water in a calibrated burette. Desorption could be carried out under vacuum or at atmospheric pressure.

Two terms will be used to denote the activity of the compound being considered. *Productivity (P)* is a term which refers to the actual amount of oxygen produced under cycling conditions. It is dependent upon the actual cycle and the conditions of absorption and desorption. By integration of a plot of productivity vs the number of cycles, the total amount of oxygen produced by a unit at any time may be determined. *Saturation (S)* is the total activity of the compound at any time and is a measure of the amount of compound present which is capable of absorbing oxygen. For Salcomine, saturation is the amount of oxygen absorbed in 1 hr at 25 C, when the agent is exposed to 1 atm of oxygen or its equivalent in air pressure. For Ethomine, saturation is the amount of oxygen absorbed in 1 hr at 25 C under 1-atm pressure of air.

Deterioration is usually expressed as per cent of original saturation, although the term *production deterioration* can be used to refer to the loss in productivity. In general, the loss in saturation does not correspond exactly to the loss in productivity, the latter being somewhat greater.

In Figure 13 are shown the results of a number of life tests on Salcomine in the ½-in. tube unit. The cycles used in these runs were derived from a standard cycle by changing one or occasionally two variables (such as absorption pressure, desorption pressure, cooling and heating fluid temperatures).

In Figure 14 are replotted the results of those runs which differ only in the desorption conditions and in the moisture content of the air used for absorption. The marked effect of low-pressure desorption is at once apparent. Changing the desorption pressure changes the equilibrium temperature at which oxygen is evolved, and if constant heating fluid temperature is maintained, the available temperature difference for supplying the heat of desorption is increased as the desorption pressure is lowered. This results in an increased desorption rate and thus it is possible to choose cycle times which will permit a minimum time of exposure of the chelate to high-temperature oxygen.

Referring to run A123 (Figure 13) in which a high (130 C) desorption temperature was used, it can be seen that deterioration is quite rapid. Deterioration brought about by exposure to oxygen at elevated temperatures is called "cooking" deterioration, and may be considered as the kind of oxidation that might go on when any organic substance is exposed to pure oxygen at an elevated temperature.

Experiments were conducted to study this cooking deterioration separately. Samples of Ethomine and of Salcomine were held at constant temperature in an air or oxygen atmosphere and periodically tested for activity. In Figure 15 are shown results for samples maintained in a desorbed condition.

On the basis of the experimental observations discussed above, it is possible to select cycle conditions in which all the factors contributing to long life and high production can be made to exert their maximum effect. "Ideal" cycles using the ½-in. tube unit were selected for Ethomine and for Salcomine. The results of life tests using the ideal cycle for Salcomine are shown graphically in Figure 16. It is seen that in this cycle 41 lb of oxygen are produced per lb of chelate to 50% of original saturation.

In Figure 17 are shown life curves for Fluomine, Ethomine, and Salcomine, the data having been obtained in tests using the ½-in. tube unit.[21] The markedly superior stability of Fluomine is evident.

11.8.6 Proposed Reactors for Use in Aircraft Wing Units

In connection with the design of a proposed aircraft wing unit for the production of oxygen in flight, using Salcomine or one of its derivatives, considerable study was devoted to the selection of an efficient, lightweight reactor. A tube bundle proved to have good performance characteristics, but considerable difficulty was anticipated in fabrication of such units. Units of this kind containing different sized tubes were compared. It was found that a ½-in. tube bundle would produce 1.3 times as much oxygen for the same weight of chemical as would the ⅝-in. tube bundle. When very thin tubes (0.020-in. wall) were used, the ⅝-in. tube bundle would produce 1.17 times as much oxygen as would the ½-in. tube bundle for a given weight of chemical plus tubes.

A finned reactor of novel design (Figure 18), built by the Frigidaire Division of the General Motors Corporation, Dayton, Ohio, is superior to the tube

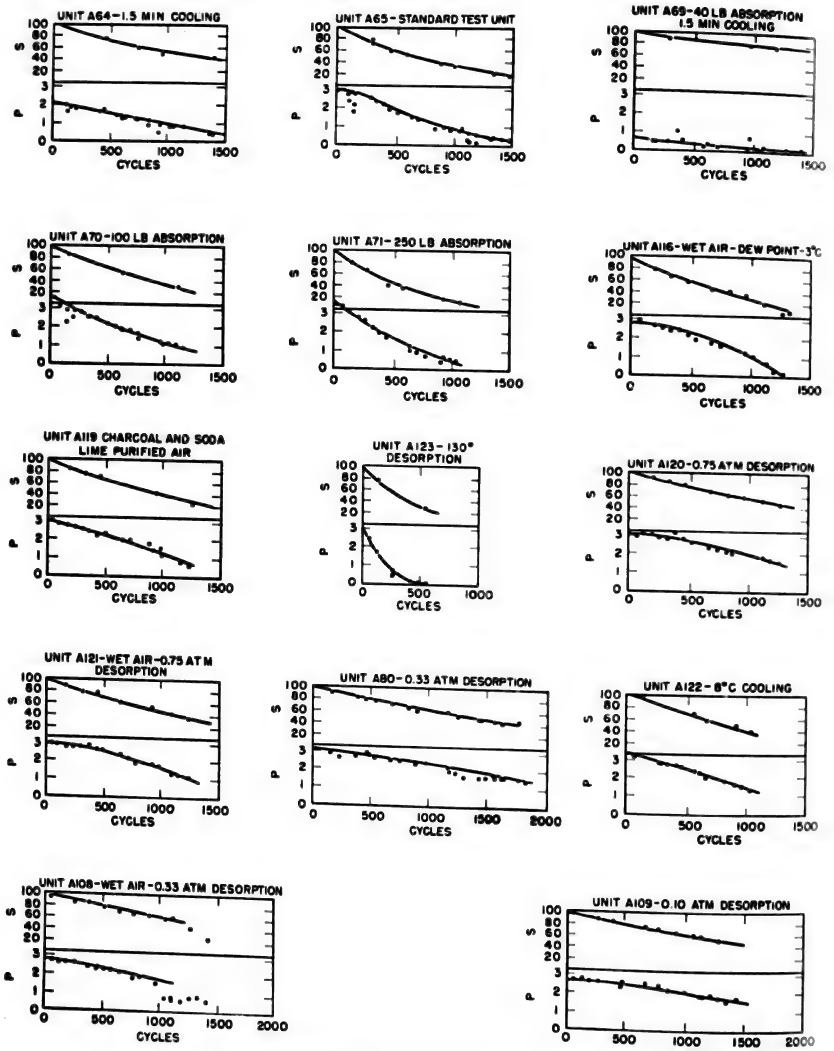


FIGURE 13. Results of a number of life tests on Salcomine.

bundle in space requirements (0.080 cu ft per lb of absorbent as compared with 0.115 cu ft per lb), and equal to the tube bundle in performance in cyclical oxygen production.

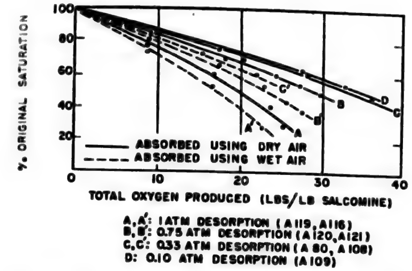


FIGURE 14. Salcomine life as a function of desorption pressure.

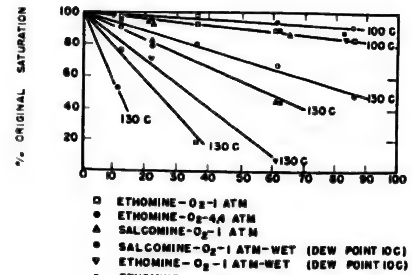


FIGURE 15. Deterioration of desorbed Ethomine and Salcomine at constant temperature and oxygen partial pressure.

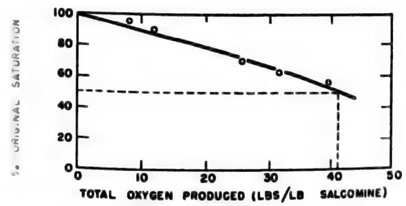


FIGURE 16. Salcomine life on improved cycle.

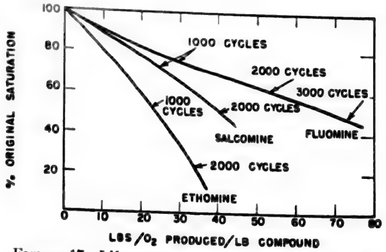


FIGURE 17. Life curves for Fluomine, Ethomine, and Salcomine.

11.8.7 Reactors Using Fins, Coils, et cetera, for Heat Transfer Surface

A variety of reactor designs were devised and tested during various phases of the developmental work. Of these the most suitable, and the one adopted for application to a prototype unit, is the so-called flat case.[33]

The flat case consists of four layers of 8 copper tubes each, horizontally disposed, ⅝-in. OD by 24 in. long, spaced 1⅝ in. on centers. Square fins (1⅝ in. square) of 0.012-in. sheet aluminum are placed six to the inch along the length of each tube. The total surface is 100 sq ft in contact with the absorbent (2.78 sq ft per lb of Salcomine). Figure 19 shows the experimental flat case, and Figure 20 shows the reactor (without the shell) designed for the shipboard unit (see below), embodying the flat-case element.

In an earlier experimental unit (Kellogg-American Machine Defense Shipboard Unit),[41,49] four reactor cases were provided, each with a heat transfer surface made from ⁹⁄₁₆-in. copper tubing wound in 24 flat spiral coils and spaced about ⁵⁄₁₆ in. apart at nearest approach. The total heat transfer surface is 134 sq ft; each case holds 160 lb of absorbent. About 30 cu ft of oxygen could be absorbed in 5 min, the rate of heat absorption thus being 32,500 Btu per hr.

11.8.8 Operating Characteristics of the Shallow Bed Reactor[33]

AIR SUPPLY VARIABLES

In general, the highest air pressure economically available should be used during absorption. This statement is subject to the following qualifications:

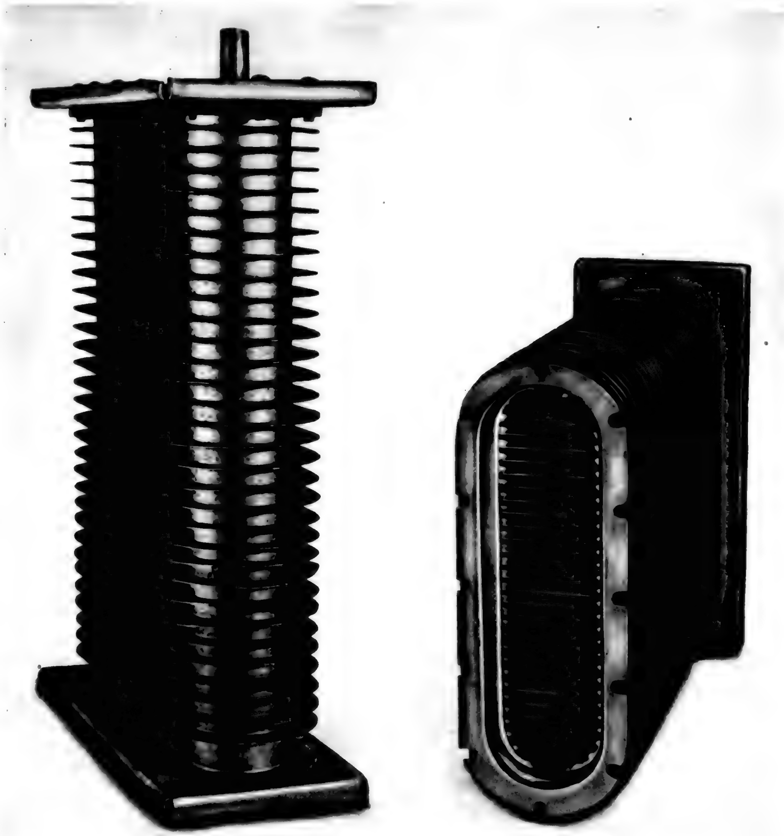


FIGURE 18. Aircraft unit reactor.

(1) the pressuring and depressuring of a case results in a mechanical disintegration of the particles of absorbent, and the use of excessively high-pressure air would result in excessive powdering of the granules, (2) the weights of metal required to withstand high pressures may become very large, increasing the heating and cooling load to some degree, (3) the loss of air on blowing down a case under high pressure is considerable.

The effect of air pressure as the only variable upon the absorption rates of Salcomine is shown in Figure 21. It can be seen that the absorption rate increases with increasing pressure, but it also appears that the rate of increase drops off at 110 psi, and that

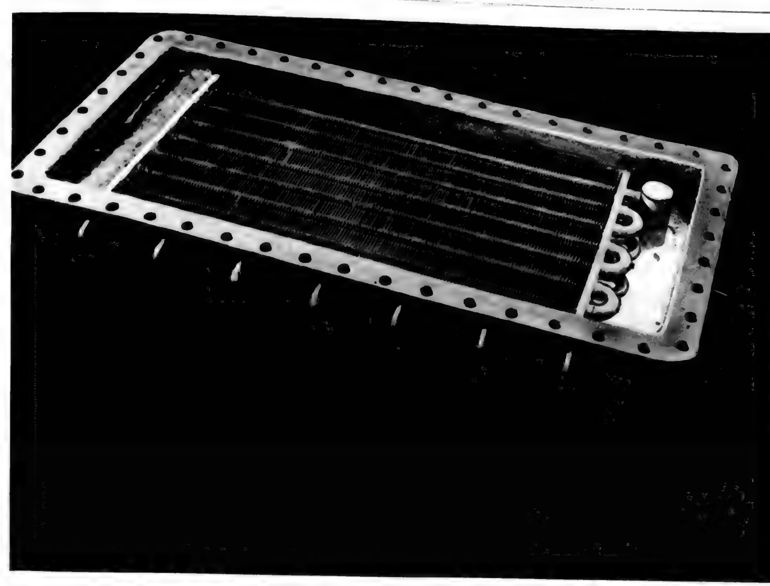


FIGURE 19. Experimental flat case.

no economical advantage is to be gained by going to higher pressures.

A study of the effect of air rate upon the absorption rate of Salcomine has shown that no appreciable increase in rate is obtained by increasing the air rate above 0.42 cu ft per min per lb of absorbent.

Air Quality. The effect of air quality (humidity, oiliness, temperature) has been investigated, chiefly in connection with life tests. The quality of the air has no observable effect upon the operating characteristics of Salcomine over a short time interval, its chief effect being on chelate life in continued operation.

Cooling Water. The cooling water temperature is an important engineering variable. Its effect has been studied, and it has been found that at low air rates (0.2 cu ft per min per lb) no marked effect is observed on raising the cooling water temperature above 50 F until about 90 F is approached. At high air rates (0.4 cu ft per min per lb) a marked diminution in yield is observed before 90 F is reached.

Heating Fluid. The desorption conditions, and particularly the temperature of the heating fluid, are of great importance both in the production of Salcomine per cycle and in its life in service.

During desorption, heat transfer is definitely the controlling variable so far as the rate of desorption is concerned. The use of a high temperature heating fluid is desirable because of the increased rate of heat transfer into the bed, the temperature of a desorbing particle being dependent only upon its oxygen content and the partial pressure of oxygen to which it is exposed.

The use of excessively hot heating fluids must be avoided, however, for two reasons. The most important of these is that the deterioration of Salcomine and its congeners is due partly to exposure to high temperatures in the presence of oxygen. Although the temperature of the *desorbing* chelate is not materially dependent upon the heating fluid temperature, after a given particle is desorbed it can reach the temperature of the heating fluid and thus undergo cooking deterioration.

The importance of using low desorption pressures

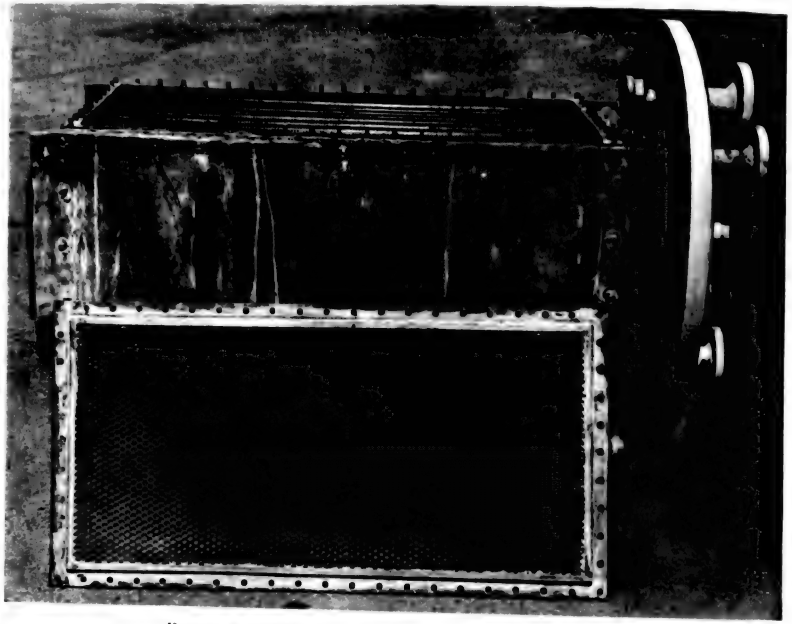


FIGURE 20. Reactor designed for shipboard unit. Shell removed.

has been pointed out in the discussion of the ½-in. tube tests. With a low desorption pressure, it is possible to use either a lower temperature heating fluid or a shorter desorption period (with a higher temperature fluid). Both of these conditions are favorable to long chelate life.

Chelate Life in Shallow Bed Reactors. It has already been shown that the life of chelate compounds of the Salcomine type is markedly influenced by the cycle conditions, and particularly by the desorption conditions.

The results of some studies on the effect of air quality and desorption pressure upon the deterioration of Salcomine in the "flat case" are given in Table 10.

11.8.9 **The Shipboard Unit**[15,16,17]

Arthur D. Little, Incorporated, and E. B. Badger and Sons Company were commissioned to design and build a unit on the basis of performance data obtained using a high productivity cycle with the high heat transfer shallow bed.

TABLE 10. Effect of air quality and desorption pressure upon the deterioration of Salcomine.

Desorption pressure	Per cent loss in activity per 10 lb O_2 produced per lb: Saturation, Dry air*	Saturation, Wet air	Production, Dry air	Production, Wet air
0.33 atm	11.0	7.3	11.7	9.6
0.50 atm	11.6	8.8	11.4	9.7
1.0 atm	13.8	25.0	10.0	17.5

* Dry air, 50 C dew point; wet air, 13 C dew point.

The reactor design was based upon the shallow bed heat transfer element and a design worked out earlier by E. B. Badger and Sons Company for use on another unit. It consists of a finned element holding 120 lb of Salcomine granules, enclosed in a tubular steel shell. A view of the inner element, with the top plate removed, is shown in Figure 20, and a complete flow diagram of the unit is shown in Figure 22.[b]

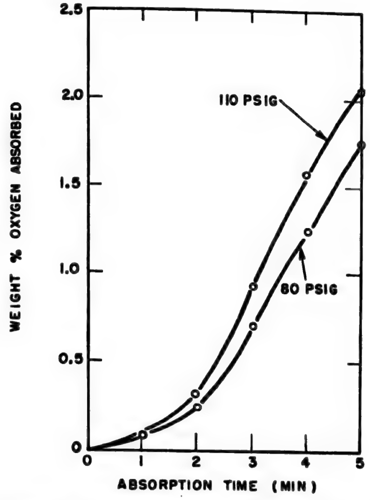


FIGURE 21. Effect of air pressure as the only variable upon the absorption rates of Salcomine.

11.9 DETERIORATION OF SALCOMINE, ET CETERA, IN CYCLIC OPERATION

The conclusions which have been reached in regard to chelate deterioration as a result of all the studies[35] (chemical and cycling tests) can be summarized as follows.

1. The deterioration of Salcomine and Ethomine in cyclic operation occurs by two distinct processes: one is associated with the production of oxygen (production), and the other with the contact of the chelate with a hot oxygen atmosphere (cooking).

2. These two processes of degradation are similar with respect to the final changes involved but are distinct with respect to mechanism.

3. Deterioration by the cooking reaction is a function of the desorption pressure and temperature. The oxygen partial pressure is involved to the 0.7 to 0.8 power for Ethomine and to the 0.4 power for Salcomine. Water vapor has no effect upon this reaction. A detailed mechanism of the cooking reaction has not been proposed, but it is supposed that the Schiff's base linkages are the labile points of attack.

4. The chemical deterioration associated with oxygen production is influenced only slightly by the desorption conditions, and appears to be the inescapable price that must be paid for oxygen production. It has been suggested that the maintenance of low temperatures during absorption will prevent the occurrence of added deterioration of this sort over what invariably accompanies the release of oxygen from the oxygenated complex.

5. Desorption at low pressures affords a considerable improvement in the ratio of saturation loss to chemical deterioration. In the ideal case this ratio is, of course, unity; and the observed ratio for 0.1 atm desorption approaches this ideal value.

6. The mechanism of the production deterioration reaction is not known with certainty, but it has been supposed to simulate a molecular rearrangement of the activated, oxygenated complex, in which the oxygen, instead of being released, attacks the Schiff's base linkage of the chelate. The direct loss of carbon as CO or CO_2 is apparently not a result of the primary step of this process. For Salcomine there appears to be no loss of the integral chelate atoms except for hydrogen, which is probably lost in further oxidative attack upon the primarily degraded molecule. Water vapor in the desorption atmosphere has only a slight catalytic influence upon the rate of *chemical* deterioration, but increases the *saturation* loss threefold.

7. The discovery of effective production-deterioration inhibitors seems unlikely, but an inhibitor for the cooking reaction may be found. It is probable that the great stability of Fluomine is due to its resistance to both types of deterioration reactions.

8. Methods of reactivating deteriorated chelate in situ have not been discovered, but it has been shown that chemically intact material can be removed by

[b] This unit was installed on a Naval repair vessel in 1943,[18] when unexpected operation in tropical waters required the addition of a refrigerated air cooler. Later, corrosion necessitated replacement of the reactor tubes. Under the severe conditions of operation, the deterioration of the Salcomine was greater than experienced in laboratory tests so that only about 4½ lb of oxygen were obtained per lb of Salcomine used; this introduced a problem of supply and recharging. In spite of these difficulties the Commanding Officer of the USS *Prairie* stated, "It is believed that the unit is an excellent one and when the mechanical difficulties are overcome will be an excellent addition to any ship."

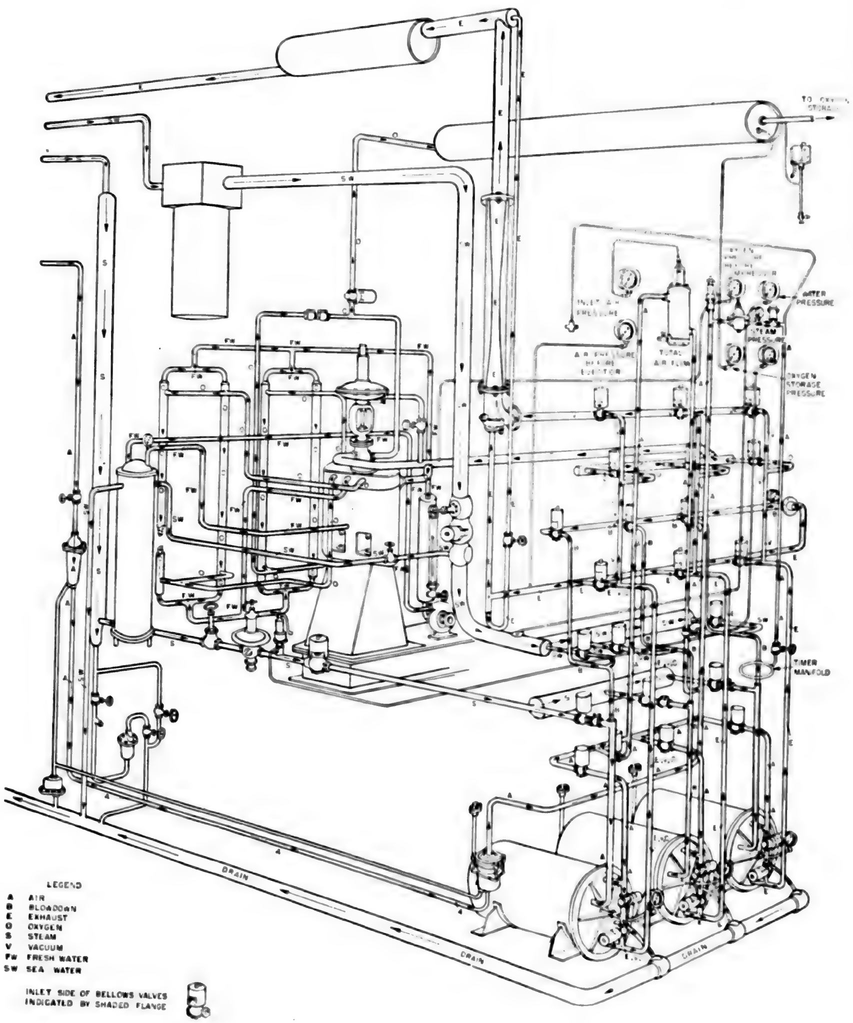


FIGURE 22. Flow diagram of shipboard oxygen unit.

solvent extraction and reactivated separately. Recovery of salicylaldehyde (or the substituted aldehyde from Ethomine, etc.) and cobalt from the deteriorated chelate is readily accomplished by acid hydrolysis.

9. For long chelate life, low desorption pressures and temperatures and good heat transfer during absorption are essential.

11.10 TOXICITY OF SALCOMINE DUSTS

It was early noted in working with Salcomine and related compounds that the dust is very irritating to the bronchial passages and to the digestive system. This prompted an investigation of the possible industrial hazards which might be involved in working with this compound.[e] Preliminary testing revealed that Salcomine dust is toxic upon inhalation or ingestion. Mice exposed for several hours to the dust frequently died within one to six days and autopsies revealed many pathological changes attributed to the Salcomine. The functions of the liver appeared to be especially affected. Similar results were obtained with larger animals such as rats, guinea pigs, and rabbits.[36,37]

Examinations made of eleven men[38] exposed to small amounts of Salcomine dust revealed that the compound produces irritation of the eyes, nose, larynx, and bronchial tubes. The symptoms which appeared shortly after exposure and resembled those of an upper respiratory infection, cleared up a short time after removal from exposure. Signs possibly indicative of mild systemic affects (muscular aches, nausea, and vomiting) appeared in some of the subjects after a latency of 5 to 24 hr.

One case with much more severe systemic affects has been reported.[39] Exposure for a short period with an atmosphere laden with Salcomine dust led to inflammation of the liver, which became progressively more enlarged. The liver condition and the accompanying jaundice gradually improved but abdominal pains still persisted. Two months later an abscess of the liver was discovered and removed. It was suspected that other abscesses were also present. A second similar abscess was removed three months later. Recovery was slow.

It is probable that the use of dust masks and general precautions taken against dust will effectively guard against Salcomine as an industrial hazard.

[e] Animal studies were made with Salcomine at the toxicological laboratory at the University of Chicago under the auspices of Division 9, of NDRC, and are reported in the summary report for Division 9 under the heading *Miscellaneous Toxicological Studies.*

Chapter 12

OXYGEN GENERATION FROM NON-REGENERATIVE CHEMICALS

By S. S. Prentiss[a]

12.1 INTRODUCTION

A SURVEY WAS made of inorganic chemical sources of oxygen that would be suitable for emergency supplies of oxygen in the field, and which also might be better adapted than the compressed gas cylinders normally available to specialized uses such as medical therapy, and cutting and welding for small isolated and infrequent jobs. The more obvious materials are listed in Table 1;[a] a number of other materials and methods have been omitted because they are less suitable from the point of view of weight per cent yield of oxygen, or the character of the reaction.

Prime consideration was given to yield of oxygen on a weight and volume basis, and also to availability. The cost of the materials was generally of secondary or minor importance, as the contemplated uses were all of an emergency character.

Two chemical sources of oxygen were outstanding because of the availability of the materials and nature of the reactions involved. These are (1) alkali peroxides, especially sodium peroxide and potassium tetroxide, which liberate relatively pure oxygen when treated with water or moist air, and (2) alkali chlorates, especially potassium chlorate and sodium chlorate, which liberate oxygen when heated. The Naval Research Laboratory did much work in the development of these materials as sources of oxygen prior to and during the NDRC program.

The peroxides permit generation on a demand basis from simple apparatus, but do require large quantities of water. Reaction with moist air, not only to generate oxygen but also to absorb carbon dioxide and water vapor, makes possible the most economical source of breathing oxygen known, the rebreather. The development of such generators and rebreathers will be discussed in the following sections.

The alkali chlorates require no water, produce pure, dry oxygen from apparatus of low weight and great density. Generators of this type are quick-starting over a wide range of temperature and are adaptable to aviation use. Modified forms of apparatus for therapeutic oxygen, cutting, welding, et cetera, were contemplated but never developed. The development of aircraft emergency equipment is discussed in a subsequent section. It should be noted that the chlorates and perchlorates of the polyvalent metals such as magnesium, zinc, and aluminum are reduced to simple oxides with liberation of part of the oxygen and all of the chlorine; they are, therefore, unsuited to oxygen generation.

A word can be said about several of the materials in Table 1. Hydrogen peroxide decomposes very smoothly and in many ways would be an ideal source of oxygen; however, it is not practical on a weight basis unless high concentrations (90%) can be utilized. In high concentration, there is some hazard in storage and transportation, especially in metal containers. Large-quantity production of high concentration hydrogen peroxide has recently been developed,[b] and container problems may some day be satisfactorily solved to maintain the weight-saving inherent in the peroxide itself.

An examination of several reversible processes (for example, the Brin process using barium peroxide, and the Tessie du Motay process using alkali permanganates) led to the conclusion that they were not competitive with other portable methods of producing 500 to 1,000 cu ft of oxygen per hr on the basis of weight of equipment and fuel required, and certainly they were not suitable for small-scale, emergency generators.

12.2 OXYGEN GENERATORS EMPLOYING ALKALI PEROXIDES

12.2.1 Chemistry of the Peroxides

Sodium peroxide is formed by the oxidation of metallic sodium in a dry atmosphere of oxygen or air. On treatment with water, decomposition takes place according to the following reaction.

$$Na_2O_2 + H_2O \rightarrow 2NaOH + \tfrac{1}{2}O_2. \quad (1)$$

The heat of reaction is 73.2 calories per gram-mole of oxygen produced.

[a] Technical Aide, Division 11, NDRC.

[b] See STR Division 11, Volume 2.

TABLE 1. Inorganic chemical sources of oxygen.

Chemical	Mol Wt	Per cent O_2 Yield	Cu ft O_2 per lb (20 C)	Heat of Reaction Cal per Mole O_2	Remarks
Lithium peroxide Li_2O_2	46.0	35.0			Not available, but offers for production have been made
Lithium tetroxide Li_2O_4	78.0	61.5			Not available (unknown?)
Sodium hydrogen peroxide Na(OOH)	56.0	28.5			Not available
Sodium peroxide Na_2O_2	78.0	20.5	2.40	73.2	Available in large quantities
Potassium peroxide K_2O_2	110.2	14.5			Intermediate stage in formation of K_2O_4
Potassium tetroxide K_2O_4	142.2	33.6	3.94	17.5	Recently available in quantity
Hydrogen peroxide H_2O_2(100 vol)	34.0	13.2	1.54	45.8	Commercial grade
Hydrogen peroxide H_2O_2(130 vol)	34.0	16.5	1.93	45.8	Most concentrated grade made commercially
Hydrogen peroxide H_2O_2(300 vol)	34.0	42.5	4.97	45.8	90% H_2O_2; generally considered hazardous to ship and store, only recently available in quantity
Magnesium peroxide MgO_2	56.3	28.4	3.32		Not available
Calcium peroxide CaO_2	72.0	22.0	2.60		Commercial product generally 80% pure
Calcium tetroxide CaO_4	104.0	46.1			CaO_2 containing up to 9% CaO_4 reported
Calacium hydrogen peroxide $Ca(OOH)_2$	106.0	30.2			
$CaO_2 2H_2O_2$	140.0	34.2			
Calcium hypochlorite $Ca(C10)_2 4H_2O$	215.1	14.9			A laboratory method
Strontium peroxide SrO_2	119.6	13.4			
$SrO_2 2H_2O_2$	153.6	31.2			
Barium peroxide BaO_2	169.4	9.45	1.10		Brin process; regenerable with air
Barium hydrogen peroxide $Ba(OOH)_2$	203.4	15.8			
$NaBO_3H_2O_2$	100.0	16.0	1.87	(40–50)	
$Na_2B_4O_7 4H_2O_2$	325	19	2.22	(40–50)	
$Na_2CO_3 1.5H_2O_2$	157	15	1.75		
Sodium chlorate $NaClO_3$	106.5	45	5.28		Available in large quantities; decomposable by heat
Sodium chlorate candle		34.5	4.03		Combustion yielding pure oxygen
Sodium perchlorate $NaClO_4$	122.5	52	6.10		Not available in large quantity
Potassium chlorate $KClO_3$	122.6	39.1	3.35		
Potassium chlorate candle		25.2	2.94		Superseded by $NaClO_3$ compositions
Potassium perchlorate $KClO_4$	138.6	46	5.38		Not available in large quantity

TABLE 2. Available oxygen from alkali peroxides.

Peroxide	Theoretical O_2 yield (Wt %)	Theoretical O_2 yield (cu ft per lb) STP	O_2 Recovery in actual practice (%)	Amount recovered in actual practice (cu ft per lb) STP	Heat of reaction (kg cal per mole O_2)	Heat of reaction (Btu per cu ft) STP
Sodium peroxide (Na_2O_2)	20.5	2.32	97	2.24	73.2	367
Mixed peroxide (54% Na_2O_2—46% K_2O_4)	26.8	3.0	89	2.27	48.1	238
Potassium tetroxide (K_2O_4)	34	3.81	96	3.65	17.5	88

Potassium tetroxide is formed by oxidation of metallic potassium in an atmosphere of dry air. This material decomposes with water according to the following equation:

$$K_2O_4 + H_2O \rightarrow 2KOH + 1\tfrac{1}{2}O_2. \quad (2)$$

The heat of reaction is 17.5 calories per gram-mole of oxygen.

A mixture of sodium peroxide and potassium tetroxide containing potassium and sodium in the molar ration of 46 to 54 may be formed from burning an alloy obtained by heating and distilling a mixture of metallic sodium and potassium chloride. The yield and heat of reaction is intermediate to that for the pure substances. The yield of oxygen production from these materials is given in Table 2. The above reactions between water and sodium peroxide or potassium tetroxide proceed readily and smoothly at temperatures somewhat in excess of room temperatures, but when cold water is used the reaction at best is very sluggish and it is necessary to supply a catalyst. One of the simplest forms of such a catalyst

is a trace of copper sulfate, which may be added to the water supply.

12.2.2 Generating Devices

A generator operating on the Kipp principle was developed. In this generator a large outer container is partially filled with water. Located in this container is a second container in which alkali peroxide is placed. A center perforated tube in the inner container connects with the water in the bottom and operates in such a fashion that withdrawal of the generated oxygen from the inner container permits entrance of water to the mass of peroxide. A solution of caustic which is formed as a by-product drains through this same tube to the main body of water in the generator. The generated oxygen issues through a pressure controlled regulator so that a constant pressure is maintained in the generator throughout the operation.

In order to prepare oxygen gas for breathing purposes, the generated product is scrubbed with water, first in the main body of water in the generator and then in an auxiliary scrubber located on the outside of the container. Cooling coils and a trap serve to remove water condensed at ambient temperature. A second regulator serves to deliver the oxygen at a desired pressure up to the pressure of generation. Figure 1 shows the general arrangement and operation of the generator. Figure 2 illustrates several systems which were investigated.[1]

Sufficient water is provided in the generator to absorb the heat of reaction so that the boiling point is not quite reached at the end of the charge. It will be observed from Table 2 that approximately 4 times as much heat is liberated per mole of oxygen generated in the case of sodium peroxide than in the case of potassium tetroxide. For this reason a generator designed to operate with sodium peroxide must

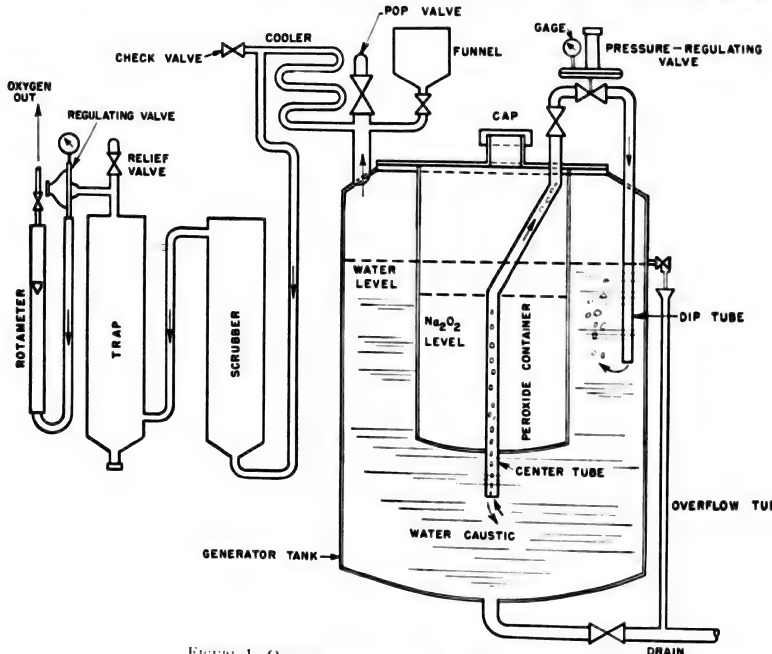


FIGURE 1. Oxygen generator—early experimental model.

be considerably larger to accommodate the excess of water required for absorbing this heat of reaction. The water required to absorb the heat of reaction is many times that required in the chemical reaction itself.

The first generator developed produces 10 cu ft of oxygen per charge and operates automatically at any set pressure from 1 to 22 psi and at any rate demanded up to 100 cfh. The outer container has a volume of 42 gal and is filled with 29 gal of water. Forty-five pounds of sodium peroxide are placed in the inner container. A second generator of smaller size was built for an emergency welding unit capable of producing 22 cu ft of oxygen from a 10-lb charge of sodium peroxide[c] (see Figure 3). The operation and general arrangement of the apparatus is similar to that described above.

A further modification provided a heavy walled vessel and suitable regulators to provide an operating pressure of 100 psi for underwater cutting operations. This unit has a capacity of 100 cu ft of gas per charge. The appearance is similar to the model shown in Figure 3.

A still further modification comprised some slight alterations permissible when K_2O_4 is used as the agent, namely, a reduction in the amount of water required and an increase in capacity of the peroxide chamber. This model has a capacity of 300 cu ft of oxygen per charge of peroxide and was further modified to provide ruggedness in the field by mounting all valves, scrubbers, etc., on the top of the container and enclosing these elements in a protecting steel cover. This apparatus was designed for use as a field unit for therapeutic administration of oxygen to twenty patients.[2] An oxygen-distributing hose is provided with constant flow fittings and masks. Each station (patient) is provided with two outlet openings of different flow rates, and the flow rate from the system as a whole can be varied by varying the delivery pressure to the hose.

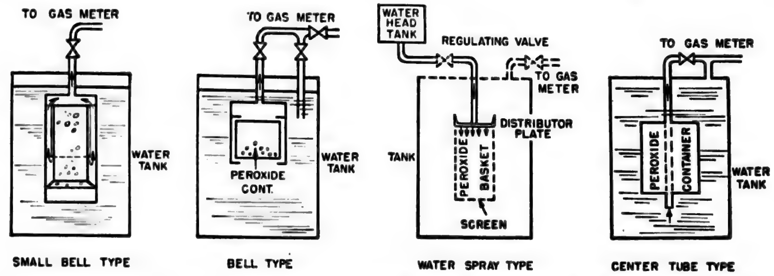


FIGURE 2. Generator types investigated for use with alkali peroxides.

[c] The experimental investigation was conducted and the model made by the du Pont Company, Electrochemicals Department. Production models and approximately 4,000 units were produced by the Sight-Feed Generator Company.

12.2.3 Rebreather Unit for Aircraft Use

INTRODUCTION

The most economical source of breathing oxygen for high-altitude aircraft use is the closed-circuit rebreather system in which oxygen is supplied and carbon dioxide and moisture are removed in compliance with the physiological requirements. Nonrebreathing systems, in widespread use, are uneconomical to the extent that gas must be delivered each minute to the lungs in an amount equal to the respiratory minute volume used. Even the most efficient non-rebreather system, in which the oxygen is diluted to an optimum degree with ambient air, requires up to 5 times as much oxygen as the rebreather system over the important altitude range from 15,000 to 35,000 ft.

In spite of the fundamental economy, rebreather systems have suffered from liabilities which have proved so serious in practice that their use in aviation practically disappeared.[4]

A consideration of some of the difficulties with earlier rebreather systems, and the attempts made to solve some of their deficiencies will show that these systems, for the most part, have been too complex

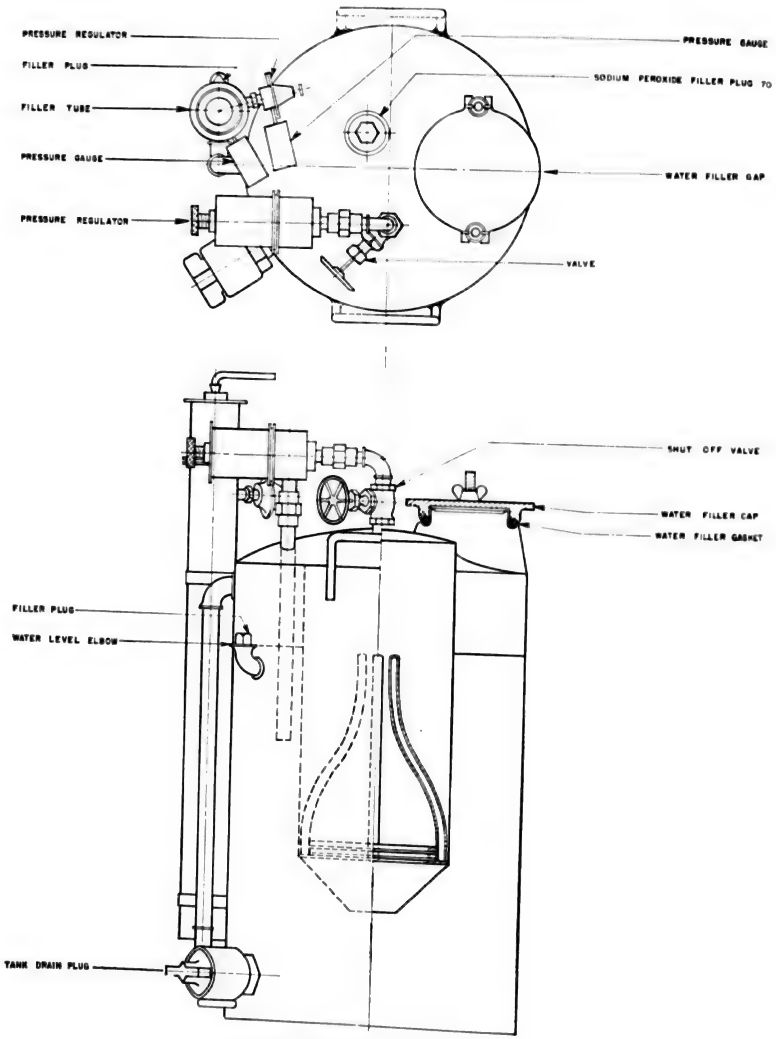


FIGURE 3. Oxygen generator 22 cu ft model.

and too unreliable for aircraft use, especially under emergency conditions.

Simple rebreathers using alkali peroxides date back to 1904.[5] In these and later rebreathers, sodium peroxide is used as the source of oxygen through reaction with moisture and carbon dioxide of the expired breath. Under the conditions of use, the oxygen was never liberated at a rate sufficient to supply the requirements of the user nor to give a margin of safety over small leaks in the system. Early workers recognized the advantage of potassium tetroxide over sodium peroxide in giving higher yields and rates of oxygen evolution, but it has not been until recent years that potassium tetroxide or the so-called mixed oxides of sodium and potassium (represented by $NaKO_3$) have been commercially available. Therefore, in these early forms of rebreather apparatus, it has been necessary to furnish an auxiliary supply of oxygen, for example, compressed gas, to meet this deficiency.

The recycled gas in the system may become diluted with inert gases, such as nitrogen, from the atmosphere through leaks or slow evolution of nitrogen from the back of tissues, and thus require purging by means of automatic small volume pumps and auxiliary supplies of oxygen.[6]

Any rebreather system which is to be used in aviation, especially if it may be required in emergency at "oxygen" altitude, must have an initial filling of oxygen and also sufficient liberation of heat to warm the chemical to a reactive temperature. Several attempts[5,7,8,9,10] have been made to improve on the Navy rebreather (electrically heated) in this respect.[d]

In the method to be described, a small chlorate candle embedded in the canister of potassium tetroxide gives off both oxygen and heat when ignited at time of use.

An improved rebreather unit known as C-K[10] was developed to take full advantage of potassium tetroxide and to provide an inherently simple system which might be stored indefinitely and used under emergency conditions and at altitudes up to 35,000 ft at ambient temperatures down to −50 C.[e]

Description of C-K Rebreather Unit

The C-K rebreather consists of a canister loaded with granular potassium tetroxide in which are embedded three chlorate candle primers with a firing mechanism. To the bottom of the canister is attached a flexible breathing bag protected by a fabric casing. Means are provided at the top of the canister for connecting a standard demand-type oxygen mask provided with a loaded expiratory valve (see Figure 4). The entire unit, with the exception of the mask

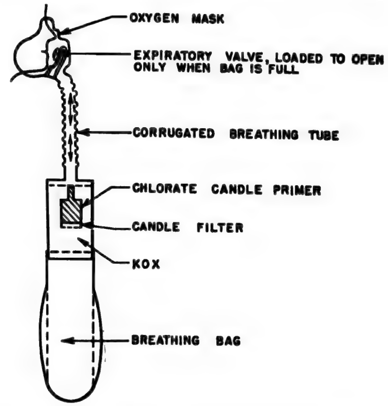


FIGURE 4. Principle of operation of C-K oxygen rebreather unit.

and connecting tubing, is hermetically sealed and compactly packaged for transportation and storage. For emergency use, a rip cord is pulled, thereby breaking the seals on the canister, freeing the breathing bag, igniting one chlorate candle primer, and disclosing the mask connection. Ignition of the chlorate candle provides oxygen to fill the breathing bag initially and supply breathing requirements for the first few minutes, and heat to warm the potassium tetroxide to operating temperature.

[d] The C-K oxygen unit is a direct outgrowth of the simplified rebreather planned and tested by Goldschmidt and Chambers, the Laboratory of Physiology, University of Pennsylvania Medical School, and constructed by Rawson in 1944. Further, it combines elements of potassium tetroxide, suitably catalyzed and granulated for rebreathers, as developed by P. Borgstrom and his associates at the Naval Research Laboratory, and of *chlorate* candles (described later in this chapter). Contributions to the development of these candles were made by the British Admiralty, the Naval Research Laboratory, the Oldbury Chemical Company, and others.

[e] Experimental units were developed by the Johnson Foundation under contract OEMcmr-26. Production models were developed and constructed in lots for experimental testing under Contract OEMsr-934. "C-K" or Candle-KOX is a code abbreviation used during development.

The five principal components of the device are described in the paragraphs which follow.

1. The face piece, with loaded expiratory valve, and associated tubing.
2. The canister proper, containing the potassium tetroxide (KOX) and housing the chlorate candle primers.
3. The candle primers with their associated ignition and filter mechanisms.
4. The breathing bag.
5. External fittings to provide thermal insulation, mechanical protection, and means of support.

used, 2½ in. thick, 4½ in. wide, and 5½ in. high. The canister contains about 300 g of the pressed and catalyzed potassium tetroxide (KOX) screened so that all particles are between 2 and 4 mesh in size.[7] The total oxygen capacity is about 200 ml of oxygen per g. With full utilization of the oxygen obtainable from the KOX, the canister should last an average man at rest for about 180 to 200 min. Due to the extra oxygen liberated by the chemical (which serves the necessary function of keeping the system flushed with fresh gas) the actual canister life is only about half this.

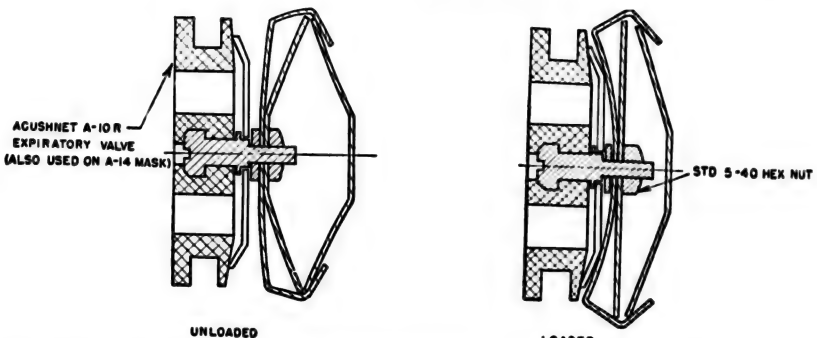


FIGURE 5. Sectional view of the Legallais optionally loaded expiratory valve. The device consists basically of a metal diaphragm so upset at its center as to have only two positions of stability, and a mechanism for changing it from one position to the other. In the "unloaded" position, the diaphragm is completely free of the mushroom valve and does not interfere in any way with its normal operation. In the "loaded" position, the diaphragm presses against the rim of the rubber mushroom valve, giving restricted opening.

The Face Piece, Valve, and Tubing. The unit is designed to be used in conjunction with the standard Army and Navy A-14 oxygen mask, or any other mask with the same connector and expiratory valve.

Use of the C-K unit requires the mask expiratory valve to be loaded to at least 5 cm of water; the loading on the regular A-14 mask valve is from 2 to 5 mm of water; if the mask is to be used interchangeably with the demand system and with the C-K unit, its expiratory valve must therefore be replaced by one having optional loading. Legallais has designed such a valve which is illustrated in Figure 5. It behaves exactly like a standard valve until the front of the mask is pressed in, which transforms it into a loaded valve. To release the loading, the mask is squeezed laterally.

Canister. A standard MSA gas mask canister is

A schematic section of the C-K unit (CK6 series as made at the Johnson Foundation) is given in Figure 6. The top carries the female connector for the oxygen mask, a simple check valve which keeps the system from losing excessive oxygen when the mask is not plugged in, supports for the three chlorate candle primers, and supporting structures for the starting and opening devices described below. In the new version with grenade fuse ignition, the canister top also carries the trigger mechanisms and percussion caps. The canister bottom is provided with a thin metal foil seal, which is punctured by a special perforator at the moment the unit is put in operation. It also supports an oval ring on which the breathing bag is bound. Screen and Fiberglas filters at top and bottom together with a spring evading device are provided to keep the KOX in place.

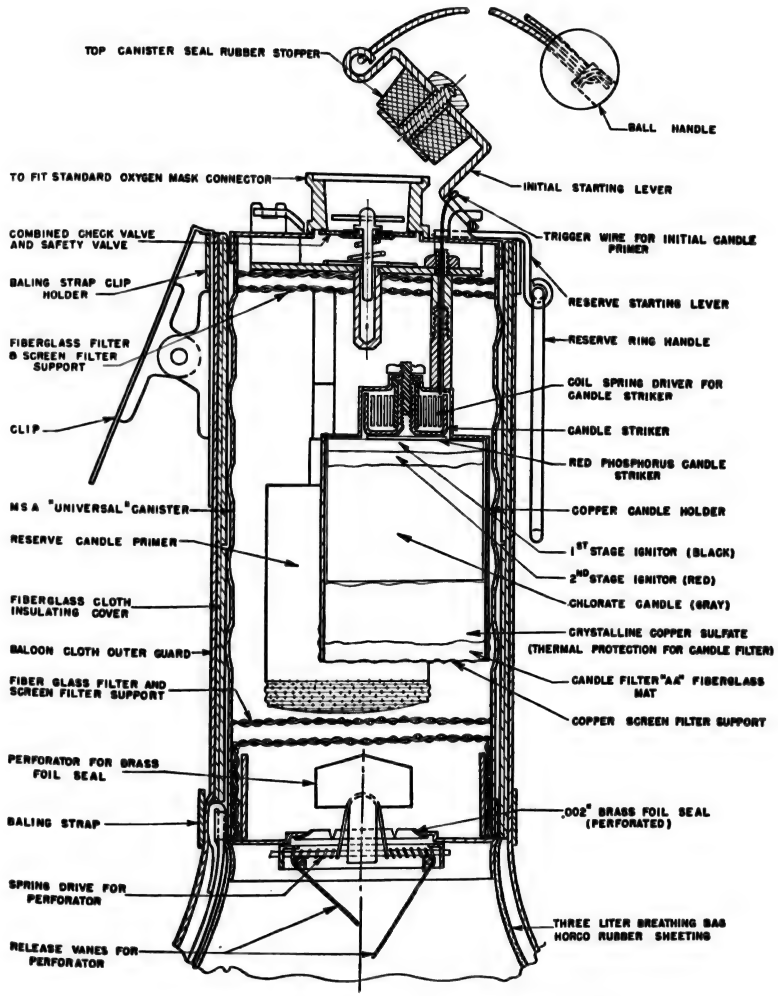


FIGURE 6. Schematic section of C-K oxygen rebreather unit.

The Chlorate Candle Primers. The three primers are identical, though one serves to start the unit in operation, and the other two act as reserves. Each consists of an outer copper case, an igniter, a chlorate candle, and a smoke filter. The form developed at the Johnson Foundation and supplied in the early sample units distributed to the Services uses a phosphorus igniter. In later units this igniter was replaced by the simpler and more reliable grenade fuze igniter developed for this purpose by the Catalyst Research Corporation. Since there are considerable differences between the two forms, both will be briefly described. They are functionally identical, except that the new form starts liberating its oxygen a little more quickly than does the old one.

In the older form, igniter and candle are housed in a flat box made of 0.010-in. copper sheet, enclosing a pressed candle of the same shape. The striker mechanism (Figure 7) is contained in a cylindrical projection at the top end of the box. It consists of a striker disk on which red phosphorus is glued, and which is screwed on to a stationary thread stud. When a piano wire trigger is pulled out by the starting lever or reserve levers, the striker disk spins down onto the candle and ignites it. The open end of the candle box is covered with two layers of Fiberglas AA mat held in place with screen and baling wire. This filter effectively removes the particles of sodium chloride liberated by the burning candle, unless its temperature rises above 150 C. To keep the filter temperature below this value some copper sulphate crystals ($CuSO_4 \cdot 5H_2O$) are placed between the candle and the filter; these absorb heat. The new form utilizing a modified grenade fuze igniter is mechanically simpler. The mechanical part of the igniter, a spring-driven hammer, is mounted on top of the canister instead of within it. The hammer strikes a conventional copper primer cap set flush in the canister top. From it a small brass tube extends inside the canister to the tubular copper spinning which serves as the candleholder. The tube contains a suitable quantity of flash mixture, set off by the primer cap and in turn igniting the cylindrical cast candle. The candle is 1 in. in diameter and about 2 in. long and weighs about 50 g. A layer of Hopcalite takes over the heat-absorbing function of the copper sulfate in the older form, and two layers of Fiberglas AA mat again act as a smoke filter. The entire primer assembly is held together by rolling the edge of the copper candleholder over the flared end of the flash tube, and the contents are kept firmly in place by a small compressi[on] coil spring.

Figure 8 gives the rate of oxygen evolut[io]n by candle primer with phosphorous ignition at a[n] ambient temperature of −40 C. In later form[s], the characteristics are much the same except that initial

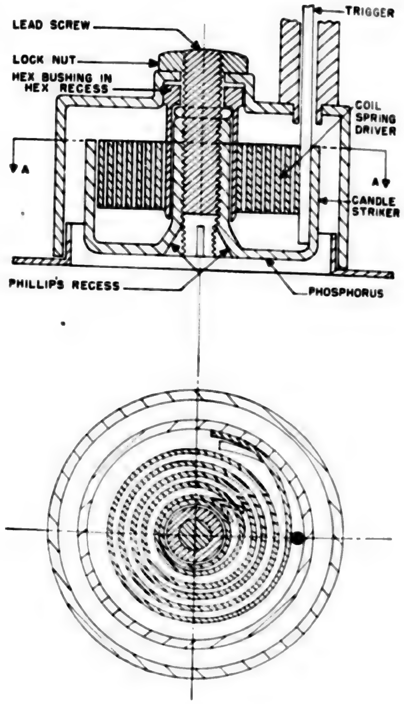


FIGURE 7. Phosphorous ignition mechanism for chlora[te] candle.

evolution is at its maximum rate so that 2 liters are produced in the first 20 seconds, instead of 1 lite[r] in the first minute. The rate of oxygen evolution by the candle is about 30% higher when the ambi[en]t temperature is 25 C instead of −40 C.

Breathing Bag. The 3-liter breathing bag is [at]tached directly to the bottom of the canister. [The]

[b]ag is made of rubber sheeting, identical to that used [i]n the diaphragms of Pioneer demand regulators (Horco No. 2796). Mechanical protection is pro[v]ided by an outer covering of balloon cloth. Both bags are of simple wedge shape, slightly larger at the bottom than at the neck.

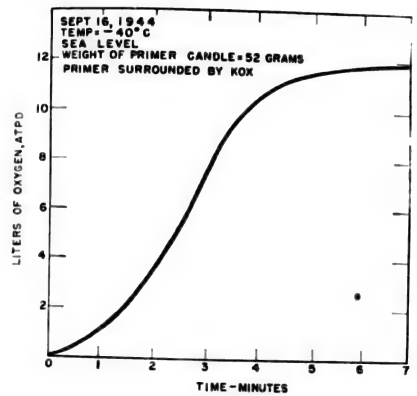


FIGURE 8. Rate of oxygen evolution by candle primer in C-K oxygen rebreather unit.

Since the bag openings are of the same area as the canister bottom, it is practically impossible to kink them in such a way as to prevent free entrance and exit of air (see Figure 9). In the packaged condition, the breathing bag is folded flat against the side of the canister where it occupies very little space.

Sealing and Starting Mechanisms. Potassium tetroxide and sodium chlorate change their properties when exposed to moisture. It was therefore of the utmost importance that the inside of the canister containing these chemicals be hermetically sealed against the atmosphere. They must, however, be instantly available for use with a minimum of handling. Seals had to be provided, therefore, at the top and bottom of the canister which would be tight but quickly breakable. For NDRC laboratory-made samples, the top seal has been merely a rubber stopper fastened directly to the starting level, which pulled free when the starting ball is pulled (Figure

This was replaced on production samples by a [cla]mped bottle cap to be positively thrown off by [the] starting lever as it is pulled away. The seal be[tw]een the canister bottom and the breathing bag consists of a disk of 0.002-in. brass soldered across a hole in the canister bottom, and perforated by a simple metal guillotine driven by a mouse-trap spring, and released when the folded bag springs away from the canister bottom, as a result of the pulling of the starting ball (see Figure 6).

FIGURE 9. C-K oxygen rebreather unit worn by a kneeling subject showing operation of reserve ring. Though the bag appears to be caught under the canister bottom it has such a wide mouth that the passage of air is not obstructed in any way.

The candle primers are ignited in the laboratory-built samples by pulling the piano wire triggers through the soft solder seals in the canister top. Fastened to their outer ends, these wires have small balls which engage with slots on the operating levers, so that the first candle is automatically ignited when the ball is pulled, while each of the reserves is ignited when its corresponding reserve ring is pulled free of the unit.

External Fittings. The metal canister is surrounded by two layers of medium-weight Fiberglas cloth as thermal insulation for the unit and for the flier. The outer cloth bag is extended up over the entire

canister to provide a neat covering, and is held in place by a simple baling strap harness which also is the anchorage for the clothes clip. A small Micarta bag guard covers the folded bag, and also hides the two reserve rings so that there will be no possibility of their being pulled until the unit is in operation.

Operation of the C-K Unit

The C-K unit is designed to be useful as an emergency or stand-by system for aircraft using the present diluter-demand oxygen installations. To serve this purpose it must withstand storage without deterioration and rough handling without damage, but must be instantly ready for use, and capable of being put into operation with a minimum amount of manipulation. When the starting ball at the top of the unit is pulled free, six actions follow automatically: (1) the top canister seal is broken by tearing off the bottle cap, (2) the connector for the mask tube is thereby freed, (3) the hammer of the initial candle primer is released to strike its percussion cap, thereby igniting this candle, (4) the bag guard is forced away from the canister, revealing the two reserve rings, (5) this also frees the breathing bag, which unfolds, (6) the perforator for the lower canister seal is released and punctures the foil which separates canister from breathing bag.

The initial primer starts to liberate oxygen at once, and should provide enough for a normal inspiration (500 ml) in 15 sec, which is little longer than the time required to transfer the mask from another system to the C-K unit. A check valve in the canister top prevents undue wastage of oxygen, if the mask is not immediately connected.

Shortly after the unit is connected, the mask expiratory valve must be loaded to about 5 cm of water or more. If a Legallais valve (Figure 5) is used in an A-14 mask, this is accomplished by merely pressing the front of the mask.

During the next two minutes, oxygen will be fed into the system at a rate of about 5 liters per minute STPD.[f] Heat is also liberated by the primer during these 2 minutes, so that by the time the candle has burned out, enough of the KOX should be warmed to a reactive temperature to take over the load of furnishing oxygen. There is thus a shift from a fixed flow emergency blast system of low economy and liberal safety margin to a chemical demand system of high economy and reduced safety factor.

[f] STPD, standard temperature and pressure dry.

Warning of Canister Exhaustion. A distinctive feature of the C-K unit is its method of warning the wearer that the canister is nearing the end of its useful life. Potassium superoxide, when used in this breathing apparatus, possesses the property of losing its oxygen-generating power before it has lost its capacity to absorb carbon dioxide. After 1½ to 2 hr of use, when the unit is near exhaustion, the expired carbon dioxide continues to be absorbed, but is not replaced by oxygen, and as a result the sensation of "striking bottom," or bag collapse at the end of inspiration, gives positive but progressive warning.

By the mere pull of a reserve ring, a second primer is at once brought into action and fills the bag. This reserve candle, like the initial one, keeps the bag full and overflowing for about 3 minutes, after which the bag begins to empty once more, reaching collapse about 10 minutes after the ring has been pulled. The second reserve primer can then be brought into play, if it has not already been used for another purpose.

It should be emphasized that the ability of the absorbing power of KOX to outlast its generating power, on which the warning system depends, is not automatically guaranteed by the use of KOX. However, in seven experiments in which bag collapse occurred while oximeter readings were being taken, the saturation was 92% or higher at the moment the warning was given. In at least six other instances, bottoming of the bag has occurred due to exhaustion of the chemical, and though saturation records were not taken, there were no subjective symptoms of anoxia.

Margin of Safety. The C-K unit has been designed for altitudes up to 35,000 ft and for temperatures down to —45 C, and it has been given tests under these conditions in the decompression chamber. The safety factor should be a little greater than that for the standard diluter-demand systems since the oxygen fraction of inspired gas is close to 1.00 instead of being adjusted to some figure between 0.21 and 1.00, depending on the altitude. The percentage leak caused by a hole of given size will be somewhat smaller for the unit than for a demand system, because while the pressure drop through the canister is about the same as that through the standard 6-ft tube used with the demand regulator (see Figure 10), the suction required to empty the breathing bag is somewhat less than that required to initiate flow from the regulator. The self-flushing feature of the unit has a greater margin of safety at altitude than at sea level.

The system could easily be converted to a safety pressure one by merely introducing a spring constraint in the breathing bag which always tended to empty it. The liability of such a system would be that small outboard leaks would tend to empty the bag and give the "collapsed bag" warning before the canister was really exhausted, thus reducing the effective life of the unit. A very low safety pressure loading might, however, prove a more satisfactory solution than the present unloaded form.

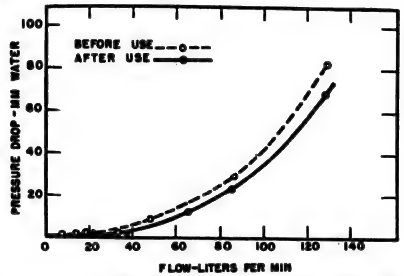


Figure 10. Flow resistance of C-K canister before and after use. Pressure drop from canister bottom to face, using A-14 mask.

Economy. The economies of a number of different oxygen systems are compared in Figures 11 and 12. It can be seen at once that no gaseous system begins to approach the economy of the C-K unit, whether calculated on a weight or on a volume basis. If the standard oxygen installation on a B-17 were replaced by enough C-K units to provide an equivalent oxygen supply (5 units per man), the total weight would be cut from 480 to 160 lb, a saving of 320 lb.

Possible Uses

The device was designed for use in aviation. Three uses have been suggested in this field.

1. As an emergency and walkabout system for planes equipped with regular demand systems (B-17, B-24, etc.).

2. As the sole oxygen system for planes with normally pressurized cabins (for example, B-29), to be used as a stand-by system in case of loss of pressurization.

3. As the sole oxygen supply for airplanes normally operating below oxygen altitudes, but which may be required to make occasional missions at higher altitudes, and in which there is no regular oxygen installation, for example, many B-25s, B-26s; perhaps some air transport operations.

Suggested Further Development. The features of the unit which adapt it to emergency conditions in the air also fit it for emergency use in mines, ships,

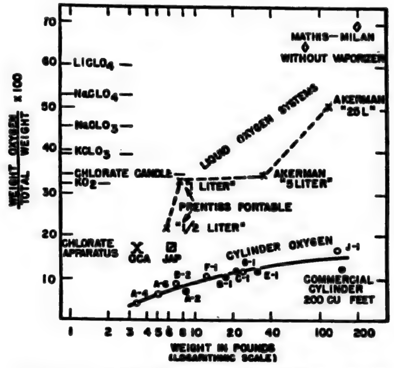


Figure 11. Weight storage efficiencies of various oxygen systems.

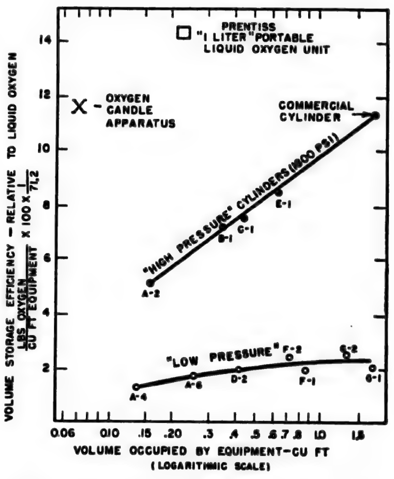


Figure 12. Volume storage efficiencies of various oxygen systems.

and gas-filled buildings. It could be used in its present form as a self-rescue unit, but for this purpose would be improved by providing a small mask or mouthpiece as an integral part, omitting the two reserve candles, increasing the bag size, and reducing the canister size to provide a somewhat shorter useful life. It is not adapted for sustained heavy work especially in warm locations, such as would be required of rescue crews, because of inadequate provision for heat dissipation and because of small canister size. Preliminary work has indicated that such a self-rescue unit will weigh (with mouthpiece) about 2 lb, measure 2 x 4 x 7 in., and have a duration of about half an hour.

Satisfaction of Physiological Requirements

Uniform Conditions. In any system making use of alkali peroxides, liberation of oxygen and the absorption of carbon dioxide are linked together:

$$2KO_2 + CO_2 \rightarrow K_2CO_3 + 1\tfrac{1}{2}O_2. \qquad (3)$$

If this were the only reaction to be considered, the picture would be simple: for each mole of CO_2 absorbed, 1½ moles of oxygen are generated. However, the situation is not as simple as this, for alkali peroxides also react with water, again liberating 1½ moles of oxygen per mole of absorbed substances:

$$2KO_2 + H_2O \rightarrow 2KOH + 1\tfrac{1}{2}O_2. \qquad (4)$$

The hydroxide formed is available for the neutralization of more CO_2, without accompanying production of oxygen.

In view of these theoretical complications, recourse was had to empirical tests of overall behavior. In a series of experiments at simulated altitudes ranging from 20,000 to 35,000 ft in the altitude chamber, the adequacy of the C-K unit to supply oxygen was checked by means of continuous gas sampling from the mask, utilizing a Pauling oxygen meter[g] or a Lilly nitrogen meter,[15] or by continuous measurement of oxygen saturation with an oximeter. The minimum recorded saturation in five experiments was 87%. The total time spent above 20,000 ft in these five experiments was about 380 min.

There is ample evidence for the efficacy of KOX as a carbon dioxide absorbent in respiratory apparatus whose configuration is much less favorable than in the present device.[12,13]

Resistance to gas flow through the canister depends upon the geometry of the system and the caking of chemical within it. The matter was carefully studied at the National Institute of Health.[13] In a number of tests of the experimental C-K units, it has given no trouble whatever. Two such tests on a single canister are plotted in Figure 10. The lack of clogging is not an indication of incomplete reaction of the chemical, since analysis of the canister material after use has shown that from 85% to 90% of the available oxygen has been liberated.

Transient Conditions. Two types of transient conditions are critical for rebreather systems: suddenly increasing activity and suddenly decreasing altitude. By the use of a large 3-liter breathing bag, and by keeping the KOX always in a warm and therefore highly reactive condition, there is provided a margin which has shown itself adequate to deal with bursts of sudden activity alternated with periods of rest.

In a sudden descent from altitude, the gas in the closed system is compressed to a smaller volume, and again there is danger that the bag will collapse completely before the deficiency is made up by the excess of gas liberated over the amount absorbed. The 3-liter bag was tested in the following way: after the unit had been in use at 30,000 ft and at −30 C for about one hour, the chamber was suddenly dived to 20,000 ft at a rate of 10,000 ft per min. The bag almost collapsed at the end of inspiration as the lower altitude was reached, but quickly filled up again. If the dive had been much faster, or had gone to a still lower altitude, it would have been necessary to pull one of the reserve rings to preserve conditions of normal respiration.

A third type of transient condition, though an artificial one, provided an even more stringent test of the device; this was the sudden replacement of oxygen by air in the bag and lungs while the unit was in operation at altitude. The record of an experiment in which this was deliberately performed is plotted in Figure 13. Simultaneous measurements were taken of arterial oxygen saturation and of the nitrogen fraction of the gas in the mask. The altitude was 30,000 ft, the temperature 0 C, and the subject had been breathing on the unit for about one hour. At a signal, the mask was disconnected from the canister and the breathing bag was squeezed flat to empty it of gas. The subject then took several breaths of air, inspired deeply, and reconnected his mask to the unit. As can be seen from Figure 13, the arterial saturation dropped from 93 to 87% during the half minute in which air was breathed, remained at about that level for the next half minute, and then rapidly rose so that within 90 seconds after reconnecting the mask the blood saturation was above the original value. The figures for concentration of nitrogen in the mask follow a corresponding course.

[g] See Chapter 14.

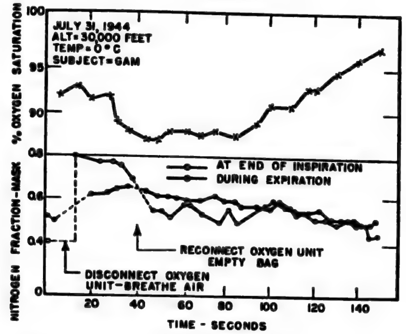


Figure 13. Recovery of subject using C-K oxygen rebreather unit after collapse of bag.

Conclusions

The tests here reported were obtained with laboratory models; units of a production model for evaluation by the Army Air Force and the Navy Bureau of Aeronautics were not available in time for inclusion in this report.

Our conclusion from the tests is that the C-K unit is adequate for both ordinary and emergency oxygen needs at altitudes up to 35,000 ft and at temperatures down to −45 C. With light activity at room temperature, the gas inspired from the canister becomes warm, but not uncomfortably so. Under conditions of sustained heavy work, such as is required of ship rescue parties, however, the inspired gas becomes unpleasantly hot and the canister gets too hot to hold in the bare hands. Over the range of temperatures usual in military aircraft at altitudes, the warmth of this inspired gas should be an asset rather than a liability.

12.3 SODIUM CHLORATE CANDLE APPARATUS FOR AIRCRAFT USE

12.3.1 Introduction

Although the decomposition of potassium chlorate was first described in 1785,[16] relatively little is known concerning its mechanism. Mellor[17] suggests depicting the reaction as follows:

$$\begin{array}{lccc} & 6KClO_3 \xrightarrow{370\,C} & KCl + 3KClO_4 + 80\ \text{kcal}, & \\ \text{or} & \Big\downarrow{\scriptstyle 370\,C} & \Big\downarrow{\scriptstyle 500\,C} & \\ & 2KCl + 3O_2 + 28\ \text{kcal} & 3KCl + 6O_2 - 24\ \text{kcal}. & (5) \end{array}$$

Little is known concerning the relative rates of reaction at different temperatures.[18,19] The decomposition of both chlorate and perchlorate is catalyzed by various metallic oxides, including MnO_2, CuO, Fe_2O_3, Co_2O_3, Ni_2O_3, and oxides of vanadium, uranium, and tungsten.[17] The rate of decomposition of $KClO_4$ as a function of temperature and concentration of catalyst has been studied by Otto and Fry,[20] who found that the reaction rate is increased about 1.6-fold for each 10 C rise in temperature. For any given reaction rate, relatively large concentrations of Fe_2O_3 are required to reduce the reaction temperature substantially.

The oxygen candle apparatus [OCA] employing sodium chlorate is a compact, portable source of oxygen designed to supply personnel in military aircraft for periods of 30 to 40 min. There are two major uses for which the apparatus is intended: (1) general purpose walk-around and emergency oxygen supply in aircraft equipped with standard demand oxygen systems, and (2) occasional or emergency use in aircraft which ordinarily require no permanent oxygen installations, such as in pressurized cabin aircraft, medium altitude bombers, and transport planes. Figures 11 and 12 show the weight and volume storage efficiencies of standard aviation oxygen cylinders now in use by the Services. Various experimental units and chemicals, including the OCA, are shown for comparison. In contrast to cylinder oxygen, the storage efficiency of liquid or chemical oxygen is relatively high, particularly in the weight and volume range of portable units.

The use of chlorate candle oxygen generators for this purpose was suggested by developments already under way at the Naval Research Laboratory for application in submarines. Sodium chlorate was immediately available in ton lots at a low cost. It therefore appeared possible to provide oxygen economically in expendable units which would require no servicing and which could be shipped, stored, and used in much the same way as tinned food.

The development of such an oxygen system for aircraft use was started late in 1943. It proceeded as a

joint project among several laboratories. The Naval Research Laboratory and the Oldbury Electrochemical Company were concerned chiefly with the development of the candle. The Mine Safety Appliances Company, under contract with Division 11 of NDRC, worked on production problems and on the development of a satisfactory ignition system. The Johnson Foundation, working under contract with the Committee on Medical Research, was concerned with physiological specifications, the design and testing of the apparatus, and practical aspects of the problem as it is related to military aircraft.

The possibility of using chlorates as a source of commercial oxygen has been extensively investigated in Germany and numerous patents covering chlorate oxygen sources and methods of use were issued in Germany, France, and Japan prior to World War II.[21] In all these applications, the high temperature required for the decomposition of the chlorates and perchlorates is obtained in part from the heat of decomposition of the chlorate itself and in part from the oxidation of accessory combustible materials mixed with the chlorate. In 1930 Hoch[22] described an individual oxygen supply unit for use in mine rescue work which utilized oxygen from a chlorate "briquette" manufactured in Berlin under the trade name "Naszogen." In 1933 the British Admiralty tested the German product as a possible means of oxygen replenishment in submarines, but the apparatus was rejected because the oxygen liberated was contaminated with chlorine.[23] In 1942 the Japanese put into military service a chemical oxygen generator for aircraft use.[24,25,26]

Exploratory experiments with chlorate generators were made in England in 1942. The material tested at this time suffered from the same disadvantage as did the Japanese and German generators, that is, contamination of the oxygen with toxic impurities.[27,28] At the request of the Naval Research Laboratory, the Oldbury Electrochemical Company of Niagara Falls, N.Y., undertook to improve the yield and purity of oxygen evolved from chlorates. The Oldbury Company arrived at the following formula:

Sodium chlorate	74%
Powdered iron	10%
Barium peroxide	4%
Fiberglas	12%

This mixture represents a considerable improvement over previous chlorate generators. The substitution of $NaClO_3$ for $KClO_3$ increases the oxygen yield. The use of reduced Fe powder in place of carbon as an accessory heat source reduces contamination of the oxygen with CO and CO_2 although some CO is still formed from organic impurities in the mix (Table 3). The introduction of an alkaline oxidizing agent (4% BaO_2) eliminates the formation of free chlorine. The technique devised by the Oldbury Company is as follows:

The dry ingredients are mixed by stirring, moistened with 5% by weight of water, and loaded into a rectangular mold measuring 9x1x1 in. Pressure of 5,000 psi is applied slowly along one side of the mold so as to compact the material transversely. After pressing, the mold is disassembled and the fragile cake dried at 100 C. After drying, the cake or "candle" has sufficient strength for handling.

The Oldbury product was tested at the Naval Research Laboratory[28] and used in the first experimental models of the OCA in December 1943. The performance was sufficiently satisfactory to stimulate the investigation of methods for large-scale production.[29] The Mine Safety Appliances Company undertook to provide material for further experiment and to investigate the properties of the Oldbury product from the point of view of production. The molded candles manufactured by the MSA Company were of value to the experimental program but the properties of the material varied greatly from one batch to the next and it soon became apparent that one or more unknown factors were present. The density of the molded candles may be varied from 1.9 g per cc to 2.2 g per cc by altering the pressure applied to the mold. However, variations in density appear to have little effect on the rate of evolution of oxygen. Increase in the quantity of water used in the initial mix decreased appreciably the rate of oxygen evolution from the pressed and dried candle.

Early in 1944 a new method of manufacture was introduced which avoided some of the variables complicating the production of uniform molded candles. The Naval Research Laboratory[30] explored the possibilities of fusing the dry mixture of ingredients and casting the molten material into blocks of the desired size and shape. The candles made by this method proved to be superior to any of the previous forms. The density, oxygen yield, strength, and uniformity were increased while the concentration of CO in the evolved oxygen was reduced to less than 0.01% (see Table 3). Furthermore, the method of manufacture proved to be more adaptable to mass production, and in December 1944 the manufacture of molded candles was discontinued in favor of the cast form.

TABLE 3. Stages in the development of chlorate oxygen generators.

			German 1930 trade-name "Naszogen"	French molded	Japanese in military service 1941–42 aircraft, Ref 9	Japanese in military service 1941–42 aircraft, Ref 10	British I 1942 molded	Oldbury Co. for the NRL 1942–43 molded	British II 1943 molded (Trial service in submarines, 1944)	Naval Research Laboratory 1944–45 fused and cast
% Composition of generating compound	O_2 source	$KClO_4$	..	40						
		$KClO_3$	..	40	76	75	72.5			
		$NaClO_3$	..	..	..	..	..	74	79	80
	Supplementary heat source	C	..	2	0.4*	.4*	Impurities	0.005*	Impurities	0.001*
		Fe	10	..	2.0	..	12.5	10	5.5	10
	Binder	Asbestos fiber	..	..	3.9	..	12.1	..	12.6	..
		Infusorial earth	..	15	..	..	..	..	..	..
		Silicious filler	..	..	..	5.3	..	..	..	..
		Fiberglas	..	..	..	..	..	12	..	6
	Other ingredients (oxidizing agents, catalysts)	Iron oxides	..	3	15.6	19.2	..	..	..	..
		Cu powder	..	..	..	..	0.8	..	0.8	..
		$NiCo_3$	..	..	..	..	0.1	..	0.1	..
		MnO_2	..	..	..	0.6	..	..	..	..
		BaO_2	..	..	..	..	2.0	4.0	2.0	4
Density g/cc			..	..	1.8		1.8	2.0	1.7	2.45
Oxygen yield		Weight per cent	..	..	27.5		25.2*	30.5	34.0*	34.1
		Vol O_2-Vol chem (liquid $O_2 = 797$)	..	..	350		320*	430	400	580
Heat of reaction		Cal/g material	..	..	210*		250*	215, 226*	185*	201,200*
		cal/liter O_2	..	..	1,100*		1,420*	1,060	730	835
Composition of evolved gas		% O_2	..	..	96 ±1		..	99	..	99.5
		% CO_2	..	..	3.5±1		..	1	..	.05
		% Cl_2	..	..	Present but adsorbed in filter		.001	0	..	0
		% CO	..	..	0.1		.08	.03	..	.007

* Calculated values.

A summary of the composition and of certain properties of chlorate candles at various stages in their development is given in Table 3.

12.3.2 The Development of Sodium Chlorate Generators

PROPERTIES OF CHLORATE CANDLES

Description of Current Candle. The chlorate candle as it is produced for the OCA is a solid cylinder 25.4 cm long and 4.1 cm in diameter (Figure 20). The candle weighs 810 to 815 g and displaces 330 cc (density = 2.45 0.05 g per cc). The interior is a gray, hard, homogeneous brittle material of about the same consistency as lava. The surface is green-brown, hard, and shiny. The melting point is 255 C and the material may be cast or recast from molten form to any convenient shape. It contains a dry mixture of the following ingredients:[h]

$NaClO_3$	81%
Fe powder (reduced with hydrogen)	10%
BaO_2	3%
Powdered Fiberglas (baked at 400 C)	6%

One end of the candle contains a built-in ignition system which will be described in a subsequent section. After ignition the reaction continues uniformly

[h] Throughout the remainder of this report, the candle compositions are abbreviated to the form $W—X—Y—Z$. Where W = weight per cent $NaClO_3$, $X = \%$Fe, $Y = \%BaO_2$, and $Z = \%$ glass.

and is visible as a thin fluid layer of incandescence which proceeds slowly down the cake, leaving a hot gray-black magnetic residue of fused salts, metallic oxides, and glass.

Action of Iron. It might be expected that the powdered, reduced iron in the presence of 100% oxygen at high temperature would be completely oxidized:

$$4Fe + 3O_2 \rightarrow 2Fe_2O_3 \; 381{,}000 \text{ cal}$$
$$(171 \text{ cal per g candle}). \qquad (6)$$

Of the oxygen available from the chlorate 12% would then be required to oxidize the iron and only 88% would be liberated as free oxygen. Actually this is not the case, for 95% of the oxygen contained in the chlorate is liberated (Figure 14). In the case of the cast candles, the oxygen yield may *exceed* the yield calculated on the assumption that all of the iron is converted to the lowest possible oxide and it must be concluded that one-third to one-half of the original iron is left uncombined with oxygen. As the concentration of iron is increased, the proportion of iron oxidized is decreased (Figure 14).

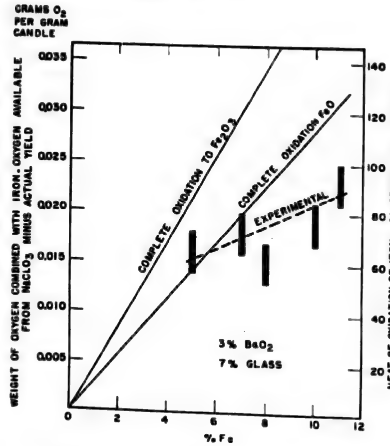


FIGURE 14. Oxidation of iron in cast candles.

For candles of any given composition, the yield of oxygen appears to be independent of the burning rate.

The conclusion that only a fraction of the iron is oxidized may be also derived from calorimetric measurements. The heat of oxidation of iron to FeO, Fe_3O_4 or Fe_2O_3 is 4.0 kcal per g of combined oxygen. The ordinates of Figure 14 may, therefore, be expressed directly in calories as indicated on the right-hand scale.

Although the increase in total reaction heat caused by an increase in the concentration of iron is unexpectedly small, it is ample to explain the change in decomposition rate. The specific heat of fused $NaClO_3$ is approximately 0.32 cal per g[31] so that, if the entire increment in heat of reaction were employed in raising the temperature of reaction, the change from 5 to 11% iron would raise the temperature about 75 C. According to the data of Otto and Fry[20] this should be sufficient to produce a 30-fold increase in the decomposition rate of $KClO_4$. In practice the rate of decomposition is limited by other factors and the change from 5 to 11% Fe about doubles the rate of oxygen evolution as shown in Figure 15. For any given diameter there is a lower limit to the concentration of iron at which the reaction will proceed reliably. For 1⅝-in. candles this limiting concentration is about 5% at room temperature.

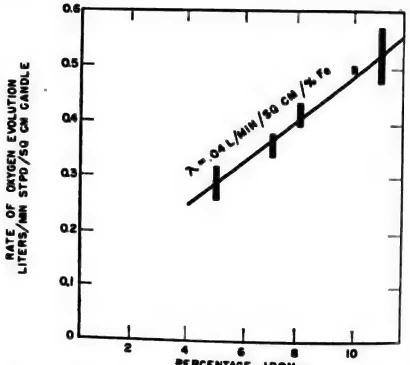


FIGURE 15. The effect of iron on the evolution of oxygen from cast candles at room temperature and constant barium peroxide concentration.

Action of Barium Dioxide. The BaO_2 was originally introduced as a supplementary agent to eliminate free chlorine evolved from side reactions.[28] It was also observed that the addition of 1% BaO_2 increases the rate of oxygen evolution by 0.04 ± 0.006 l per min per cm², an amount which is indistinguishable from the effects of a similar change in the con-

centration of iron. Figure 16 shows the relative effect of BaO_2 and Fe on the *maximum temperatures* attained by thermocouple walls inserted into the candle.

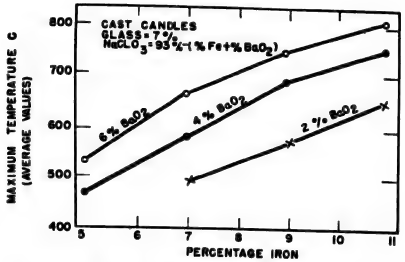


FIGURE 16. Effect of variation in the concentration of iron and barium peroxide upon the maximum temperature of combustion (ambient temperature, 25 C).

The concentration of glass may be varied from 6 to 15% without appreciably affecting the burning rate of the chlorate candle. When the concentration is reduced below about 5% the cast candles tend to develop cracks during the cooling and hardening process. The glass used for the present candles is standard Owens-Corning "curly wool" Fiberglas. It is baked at 400 C before use in order to remove organic impurities, the incomplete oxidation of which leads to contamination of the oxygen with CO.

Moisture. The candles are slightly hygroscopic and the rate of burning is slowed in candles containing appreciable quantities of water. However, cast candles have been stored under room conditions in temperate climates for six months with the absorption of less than 1 g of water, and with no detectable change in oxygen yield or burning rate. Under conditions involving large changes of temperature and pressure, precautions against the absorption of water must be considered.

Physical Factors Affecting the Rate of Oxygen Evolution. Factors affecting rate of oxygen evolution are as follows.

1. Heat conduction and burning rate. For candles of any given dimensions and composition the rate of oxygen evolution is determined by the temperature of the reactants immediately ahead of the burning front. Physical factors affecting the transmission of heat from the burned portion of the candle to the unburned portion may greatly alter the rate of oxygen flow.

Figure 17 shows the effects of different conditions of insulation and heat conduction on the temperature of the unburned material below the incandescent front. In the experiment of curve I the conditions were such as to favor the transfer of heat from the hot residue to the unreacted portion. The candle was enclosed in a copper container, buried under six inches of insulating material (Vermiculite), and the hot oxygen allowed to pass over the unreacted chemical. Under these conditions the temperature (as recorded by Pt-10%Rh insulated thermocouples inserted into the center of the candle) rose to the melting point 13.5 mm in advance of the incandescent front and the rate of oxygen evolution averaged 12 l per min STPD. In the experiment of curve III the candle was ignited in the open air; in this case the internal temperature did not rise to the melting point until the incandescent front was 5 mm distant, and the oxygen flow averaged only 5 l per min STPD.

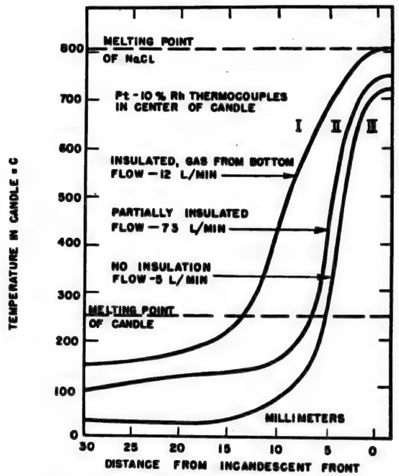


FIGURE 17. Heat conduction in cast candles.

2. Candle diameter and flow rate. It was found that the rate of oxygen production per unit area diminishes slightly as the candle diameter is increased although the relation between flow rate and area is approximately linear in the experimental range.[30] The maximum temperature reached by the residue increases slightly with diameter; presumably this

results from a diminished surface to volume ratio available for heat loss.

3. Low temperature. The performance of chlorate candles equilibrated with low temperatures is of particular importance to their application in aviation. It was found that for $1\frac{5}{8}$-in. diameter candles in the range of temperatures −55 to 25 C, the change in oxygen production is about 0.02 l per min per degree. Failures are likely to occur at −50 C among candles containing less than 9% Fe and 4% BaO_2 or when no insulation is provided.

4. Absolute pressure. Under isothermal conditions the reaction rate is independent of absolute gas pressure over a wide range of values as shown in Figure 10. This is of practical importance in the design of equipment which is required to operate at altitude or where it is desired to use chlorate to refill oxygen cylinders under pressure. If the heat from the compressed oxygen is distributed to the unburned section of the candle, the rate of oxygen evolution may be greatly accelerated.

5. Mechanical pressure and vibration. The candle substance is fluid at the site of reaction and the burned portion of the candle is easily separated from the unburned portion, thereby interrupting the conduction of heat and stopping the reaction. The oxygen flow may be slowed in graded fashion by mechanical forces tending to separate the two ends of the candle; vibration (1200 cpm) or even slow shaking may greatly slow the reaction. Steady mechanical compression up to 10 psi between the two ends of the candle has little effect on the burning rate, although the candle may be "squashed" by such a procedure to four-fifths of its original length.

Remarks on the Constancy of Flow. When candles of $1\frac{5}{8}$-in. diameter are burned under conditions such that the mean flow rate exceeds 4.5 l per min STPD, the variations in flow rate integrated over any one minute do not ordinarily exceed 0.5 l per min. However, there have been exceptions to this generalization, notably in candles of composition 81-10-3-6 burned in tin containers, where the flow rate has fallen to one-half its rated value for periods of 30 to 60 sec.

The Ignition System

The development of a simple method of igniting the generating compound which would operate reliably at −60 C and at altitude proved to be unexpectedly difficult. Much work was done in developing a three-stage ignition system in which the first stage was ignited by frictional contact with red phosphorus. This method had several deficiencies which were never satisfactorily remedied. The most serious of these—and also the most difficult problem to approach experimentally—was its unreliability. At one stage in the work over 200 consecutive samples were ignited at −50 C without failure. This record of success was followed by a long series in which the number of failures ranged from 0 to 8 out of 10. There is little question that the problems involved in phosphorus ignition could eventually be solved, but the necessity for work along this line was obviated by the introduction, in November 1944, of a percussion igniter of the hand grenade type. The modified hand grenade bouchon (developed for the Mine Safety Appliances Company by the Catalyst Research Corporation) is available at low cost and the reliability of similar units used for munitions has already been proved on a large scale.

The ignition system built around the grenade fuse is shown semi-diagrammatically in Figure 18. The ignition takes place in six stages as shown in the figure. The first three stages occur within the grenade and produce a flash which dissipates about 800 cal in the course of 0.1 sec.

A relative measure of the efficiency of energy transfer from the grenade to the candle primer may be made by determining the temperature of a copper disk of known weight inserted in place of the candle primer. Such a disk will absorb about 180 cal, indicating that the efficiency of transfer of energy is about 22%; presumably the remaining heat is dissipated in the walls of the container. The transfer of heat by the grenade flame to the primer is markedly reduced at altitude. Primers which were reliably ignited at sea level occasionally failed at altitude and measurements with the copper disk technique showed that the energy transfer was reduced by about one-third at a pressure altitude of 50,000 ft.

A series of 100 units of the configuration and composition shown in Figure 18 has been run without failure at a pressure altitude of 50,000 ft and at −55 C. The flow rates were measured in 15 cases and a statistical analysis of the results is shown in Figure 19. The results appear to justify the belief that this form of ignition is reliable. However, experience with phosphorus ignition has shown that a statement of reliability cannot be made from 100 units. It should be noted that three out of six units failed to operate when the temperature was further reduced to −70 C.

The total heat liberated by the ignition system is approximately 17 kcal (grenade fuse 0.8, primer 4, cast cone 12 kcal) in the course of one minute. This is in contrast to the candle proper, which liberates heat at the rate of about 4 kcal per min. This rapid evolution of heat from the igniter cones gives rise to two problems.

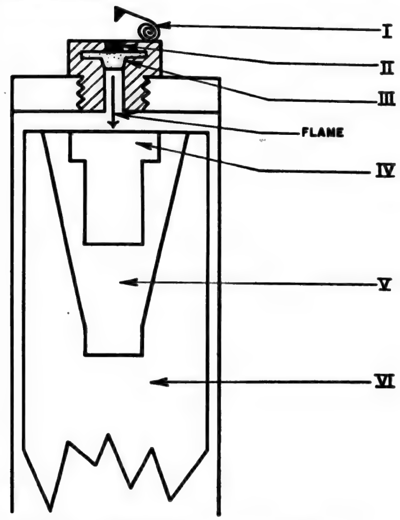


FIGURE 18. The ignition system of modified hand-grenade bouchon.

I. Percussion (hammer released by drawing cotter pin).
II. Explosive mixture 35 $KClO_4$, 30 Sb_2S_3, 21.512 mg; 15 $CaSi_2$, 3 TNT in gumarabic, binder.
III. Flash powder mixture of Ti, Ni, and $KClO_4$, 0.6g. Flame such that no free O_2 is evolved.
IV. Primer pressed mixture (37 Fe, 3 Zr, 10 BaO_2 $NaClO_3$ 20 glass); 8 g mixed with 7% H_2O and dried.
V. Cast cone 20 Fe, 60 $NaClO_3$, 10 BaO_2 10 glass; 37 g embedded in candle.
VI. Candle proper 10 Fe, 80 $NaClO_3$, 4 BaO_2, 6 glass.

1. The maximum temperature reaches 900–1000 C. This exceeds the melting point of NaCl (804 C) and the evolution of oxygen causes violent ebullition and splattering of the molten material. It is therefore necessary to introduce a brass splatter guard directly over the ignition cones in order to prevent clogging of the filters.

2. The top of the container may reach red heat (500 C or more) unless sufficient heat capacity is present.

It is of interest that the Japanese ignition system also employs a cone of highly reactive iron-chlorate mixture embedded in the generating compound; in this case, however, the cone is ignited via a series of fuses which are initially fired by a hot wire operated by the aircraft's electrical supply.

The candle substance is not easily ignited with an open flame. Once started, however, it will contribute violently to any general conflagration. Preliminary gun-fire tests carried out at Wright Field indicate that incendiary bullets will not ignite pressed candles containing 6 to 8% iron, but may ignite the 12% composition. No data of this nature have yet been obtained using standard OCA units containing cast candles.

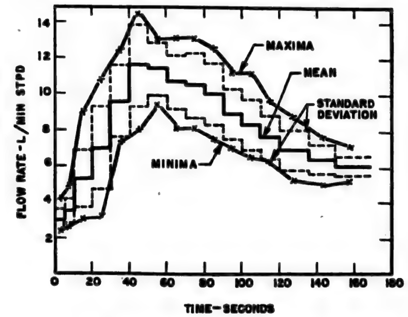


FIGURE 19. Statistical test of the ignition system of chlorate candles.

Purity of Oxygen

In addition to oxygen the evolved gas contains impurities in the form of a fine suspension of NaCl "smoke" and traces of CO_2 and CO.

CO_2 *and* CO. As shown in Table 3 the concentration of CO_2 from the cast candles is less than 0.05% and the concentration of CO is approximately 0.007%.[1] These low concentrations are in contrast to earlier chlorate oxygen generators which liberated relatively large quantities of these impurities (Table 3). Since the deleterious physiological effects of CO depend primarily on the ratio of the partial pressures of CO to O_2, this concentration is too small to produce measurable physiological effects.

[1] As estimated with the National Bureau of Standards Calorimetric CO Indicator.

NaCl *Smoke.* Each liter (STPD) of evolved oxygen contains approximately 5 mg of a fine suspension of NaCl particles. This smoke may be removed by filtration; the most satisfactory filter found for this purpose is a fine Fiberglas mat which, after baking at 400 C, is free of organic impurities. (AA Fiberglas mat, fiber size ½ micron diameter, manufactured by Owens-Corning Fiberglas Company, Toledo, Ohio.)

Impurities from the Ignition System. The flash powder (0.6 g) is quantitatively transformed to NiO, TiO_2 and KCl and these materials are deposited on the surface of the candle and on the inner walls of the container. The nickel contains about 1% Hg as an impurity. The total quantity of mercury from this source is about 1.8 mg. It is unlikely that this amount could produce symptoms of mercury poisoning in humans, even supposing all of it to reach the inspired gas once each day for two months.[32] However, should this prove advisable, mercury-free Ni may be substituted for the present impure material.

The oxygen liberated from the primer and cast cone is contaminated with about 0.01% CO.

12.3.3 Apparatus

Factors Determining Design

The chlorate candles described in Section 12.3.2 may be used as a source of oxygen for a variety of purposes. However, each application may require the development of specialized equipment, the design of which is dependent partly upon the requirements of the problem and partly upon the decomposition characteristics of the candles. The following section is concerned with one such application, namely, the development of an expendable apparatus to provide a portable emergency oxygen source for aircraft personnel equipped with standard demand masks.

General Scheme. The general design and arrangement of parts is shown in Figure 20. Candle *A* is contained in a thin-walled metal container *B* from which it is insulated thermally by glass fiber *C*. Mounted in the upper end of the container and directed toward the sensitive primer *P* of the candle is a bouchon-type igniter *D* (see also Figure 18). In the top of the container *B* is located a gas take-off *E* leading to a flow indicator *F* and a hermetically sealed valve *V* which permits isolation of the candle from the ambient atmosphere until time of use. Igniter *D* and valve *V* are both released by rip cord *R* at time of use. Between the candle *A* and the gas take-off *E* is a filter for removal of impurities (as discussed under Section 12.3.2) and a heat reservoir *H*. The latter is intended to absorb excess heat generated during the ignition phase. After leaving valve *V*, the generated oxygen is conducted through a tube *T* to an economizer *G* which adapts the constant flow of oxygen to the intermittent requirements of breathing. The economizer is provided with a standard connection *J* for demand masks. Inasmuch as the container *B* may attain a local surface temperature of 400 C, a guard *K* is provided for protection of hands and clothing. A flow indicator *F* is provided for ascertaining continuously the delivery of oxygen; the oxygen reserve is indicated by the color of a temperature-sensitive paint along one side of the container *B*. The entire apparatus weighs 3 lb, 14 oz (of which 1 lb, 13 oz is candle) and may be fastened to the clothing by a standard spring clip.

Details of Structural Elements

Candle and Insulation. The cast candle is 10 in. by 1⅝ in. diameter and of composition 81-10-3-7. As shown in a preceding paragraph, the reacted and unreacted portions of the candle must be rigidly held in place in order to insure a constant flow of oxygen under conditions involving vibration or mechanical shock. In the present apparatus, the candle is supported by the container *B* and a firm packing of glass wool, together with supports at each end. It is likely that the candle, thus supported, will not be injured by shocks in storage or in use, short of actual damage to the casing.

The glass fiber packing surrounding the candle serves two purposes in addition to supporting the candle. The first is to filter from the generated oxygen much of the smoke formed in the decomposition of the chlorate. The second purpose is to provide thermal insulation between the candle and the metallic wall of the container, thus preventing the transfer of heat from the hot reaction zone down the metal wall to the unreacted portion of the candle. This prevents acceleration in the rate of evolution of oxygen which otherwise occurs when the chlorate composition is preheated in advance of the zone of decomposition (Figure 17). For the same reason, the hot evolved oxygen is not permitted to pass in contact with the unreacted material, and provision is made to withdraw the oxygen from the reacted end of the candle.

Candle Container and Protective Casing. The candle chamber *B* is made from brass tubing 11¼ in.

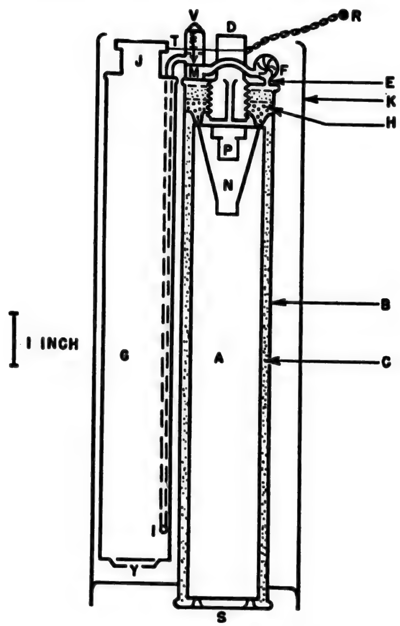


FIGURE 20. The oxygen candle apparatus [OCA].

A. Candle proper
B. Metal case—brass or tinplate
C. Fiberglas filter, insulator and shock absorber
D. Grenade ignition bouchon
E. Gas take-off
F. Flow indicator (spinner)
G. Economizer
H. Heat absorber (Hopcalite or $KClO_4$)
I. Oxygen inlet to economizer
J. Standard connection for mask hose
K. Micarta-cork outer case
M. Diaphragm for hermetic seal
N. Ignition cone
P. Primer
R. Ripcord for starting ignition and breaking seal
S. Blow-out patch, 50-80 psi
T. Tube from seal valve to economizer
V. Scale valve-containing spring-actuated lance for puncturing *M*
Y. Diluter valve (A-13)

long and 1⅞ in. in diameter. For the production models NDRC had hoped to use 0.015-in. tinned iron sheeting, double seamed and brazed to give hermetical sealing. This proved to be unsatisfactory, largely because the increased heat dissipation through tin plate slowed the burning rate of the candles, the composition of which had previously been determined from their behavior in experimental brass burners. Some thought has been given to the use of 0.006-in. stainless steel which could be fabricated by welding. Any of these materials can be used provided that suitable adjustments are made in the candle composition to compensate for changes in heat dissipation.

The chamber is capable of withstanding several hundred psi; however, a safety disk *S* designed to burst at 50 to 80 psi is provided at the bottom of the container in order to avoid a hazardous rupture in the event of failure of the seal valve or accidental plugging of the oxygen outlet.

The candle chamber is surrounded at a distance of ½ in. from the surface by a perforated fiber

(Micarta) guard mounted on supports of low thermal conductivity. The outer surface of the Micarta guard is coated with cork. The cork surface becomes unpleasantly warm during operation of the unit at room temperature and in still air; however, it may be handled with bare hands without serious discomfort under these conditions. At ordinary operational temperatures +10 to −10 C the surface temperature is pleasantly warm. The Micarta-cork combination is the best of a number of materials which have been considered. An earlier solution of this problem involved a water jacket and fiber cover. In this form of the apparatus approximately 140 ml of water are evaporated from the jacket, thus absorbing 75,000 cal or about one-half the total reaction heat.

Heat Reservoir and Filter. The experimental models of the OCA were provided with a heavy brass head assembly used for recharging the unit. This had sufficient heat capacity to prevent excessive heating of the apparatus during the ignition phase. In the lighter, expendable production model, however, a supplementary heat absorber is required. This is the primary purpose of the Hopcalite or $KClO_4$ introduced below the filter (Figure 20-*H*). Twenty-five grams of these materials absorb about 3 kcal in the range 0 to 500 C, and this appears to be sufficient to prevent the apparatus from reaching red heat (500 C).

Located in the top of the chamber (Figure 20) between the candle *A* and the heat reservoir is a filter comprising wire screen disks which enclose two layers of AA Fiberglas mat. This filter removes the NaCl smoke which is produced by the igniter cones or which otherwise escapes the glass mat surrounding the candle. A splatter guard is placed directly over the ignition cones in order to prevent clogging of the heat reservoir and filter with molten material from the igniter.

The filtration pressure during the operational phase is of the order of 5 to 15 psi depending on the altitude and the duration of use. During the ignition phase the pressure may be as high as 25 psi at the time of peak flow. At altitude the increase in (ambient) flow rate increases the filtration pressure and tends to maintain the absolute pressure within the container at a constant value.

Igniter, Hermetic Seal Valve, and Rip Cord. The igniter bouchon of the hand grenade type (see Section 12.3.2) was machined from brass in order to withstand the intense heat during the ignition phase. Alongside the igniter is located the seal valve *V* containing a thin metal diaphragm *M*. Above the diaphragm is a spring-loaded lance normally restrained by a pin. The lance mechanism is enclosed in a gas passage conducting the oxygen to the economizer *G*. The passage is further sealed from the release pin aperture by a gasket upon which the lance mechanism seats after release.

The release pins for the igniter and seal valve are aligned and connected to a common rip cord, which also engages a dust cover for the top of the apparatus. The seal valve is arranged to open ahead of the firing of the igniter so as to preclude pressure buildup in the candle chamber.

Flow and Oxygen Reserve Indicators. The flow indicator consists of a small propeller or pinwheel in the oxygen stream. It occupies a chamber provided with a transparent, heat-resistant mica window. Every other blade is painted with heat-resistant aluminum paint and oxygen flow is indicated by flicker as the blades rotate. The chamber is included in the hermetically sealed part of the system in order to protect the moving parts from corrosion.

The oxygen reserve indicator is a strip of temperature-sensitive lacquer (Tempilaq) painted on one side of the candle chamber. As the reaction front proceeds down the candle, the painted strip on the outside of the container melts to the level of the front. The height of the painted strip is therefore a measure of the oxygen reserve. Since the temperature gradient is very large (see Figure 17) the choice of paint is not critical. Tempilaq, which melts in the range 175 to 250 C, will indicate the oxygen reserve within 10%, at all relevant ambient temperatures.

Layering Economizer. The generated oxygen passes from the candle chamber *B* through flow indicator *F*, seal valve *E*, and connecting tubing *T* to the oxygen inlet *I* of economizer *G*.[33] It consists of a cylindrical reservoir 25 cm long and with a fixed volume of about 300 ml. The reservoir is provided at the bottom with the inlet *Y* for the source oxygen flow and a "diluter" valve inlet *M*. The latter inlet communicates with air via a standard A-13 inspiratory valve, loaded to about 2 mm H_2O to prevent outboard leakage of oxygen. Connection with the demand mask is made with standard fittings *J* at the top of the reservoir.

The economizer operates as follows. During expiration, oxygen from the candle displaces the contents of the reservoir through the expiratory valve at the mask. Oxygen stored in this way during expiration is then utilized during the succeeding inspiration.

The volume in the inspiratory tube and in the mask (120 ml) is included in the functional storage system (total volume of 420 ml).

The physiological characteristics of the system are shown in Figure 21. For example, reference to the

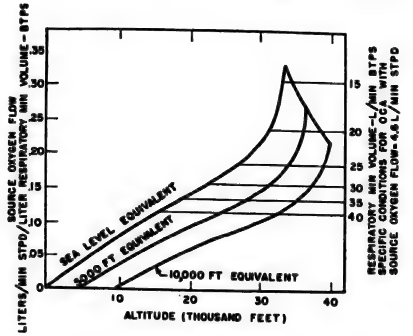


FIGURE 21. Oxygen requirements based upon the layering economizer. (Note: The oxygen candle apparatus is designed to conform to the right-hand ordinates.)

right-hand ordinate of Figure 14 shows that an individual with a respiratory minute volume [RMV] of 25 l per min BTPS using the OCA at an altitude of 27,000 ft will be at a physiological altitude equivalent to sea level. It is evident that under most operational conditions (20 to 30,000 ft, respiratory minute volume 15 l per min or less) the OCA provides more than sufficient oxygen to maintain physiological conditions equivalent to sea level. The chief advantages of this form of economizer over the conventional flexible bag are (1) greater compactness and ruggedness, (2) reduced fire hazard, (3) freedom from danger of collapse during use, and (4) no deterioration in storage.

An important limitation which this economizer shares with other free flow systems arises from the respiratory response to anoxia. If, for example, the source flow is set to maintain an altitude equivalent of 12,000 ft with a respiratory minute volume of 40 l per min (present apparatus) the resulting anoxia may cause an increased minute volume which, in turn, increases the equivalent altitude and sets in motion a cycle leading to respiratory distress and collapse. For steady state conditions, therefore, it is important to limit the use of the equipment to conditions in which little hyperventilation is likely to occur.

The layering economizer provides a simple answer to the problem of adapting the constant flow of oxygen from the candle for use with standard demand masks. However, it does so at a considerable sacrifice in *delivery* efficiency and this is particularly true under conditions of minimal respiratory activity at moderate altitudes where only a fraction of the oxygen provided by the candle is actually required to enrich the inspired gas. This is shown in Table 4,

TABLE 4. Efficiencies of portable oxygen systems under certain operational conditions.

			Storage efficiency		Delivery efficiency	Overall efficiency	
			Weight O_2	Lb O_2	Metabolic O_2		
	Weight (lb)	Duration (min)	Weight equip × 100	Cu ft equip × 1.40	Supply O_2	Man-min per lb equipment	Man-min per cu ft equipment
Standard A-4 walk-around with A-13 regulator	3.1	7	4	1.3	14	2.3	50
Experimental C-K rebreather emergency oxygen unit	3.5	90	11	8.4	c40	26	1,500
Oxygen candle apparatus present form	3.8	30	16	11.6	16	8	400
Standard A-6 walk-around with A-12 regulator	5.1	24	6	1.7	20	4.7	100
D-2 cylinder with A-12 regulator	7.1	50	8	2.1	20	7	120
A-2 high pressure with A-9 constant flow regulator	8.7	50	7	5.2	20	6	320
NDRC experimental liquid oxygen-1 liter portable with arc A-12	7.7	200	36	14	20	26	800
Modified OCA for moderate altitudes, BLB mask (not built)	2	30	18	21	23	15	1,200

Assumptions. Altitude, 25,000 ft; temperature, 25 C; physiological activity *light work* equivalent to respiratory minute volume [RMV] 20 l per min BTPS or 5.6 l per min STPD; metabolic oxygen consumption, 0.8 l per min; oxygen flows, OCA 5.0 l per min; A-13, 5.6 l per min; A-12, 4.0 l per min; A-9, 4.0 l per min. NOTE: The overall efficiency of the OCA is independent of RMV whereas the efficiency of all other systems listed is inversely proportional to RMV.

which summarizes the storage, delivery, and overall efficiencies of various oxygen systems under certain operational conditions. It is seen that in spite of the sacrifice of delivery efficiency, the overall efficiency of the OCA in terms of man-minutes per unit weight or volume is considerably greater than that of present equipment. However, it is considerably less than that of the chlorate-primed KOX unit (rebreather unit for aircraft use) or of certain liquid oxygen supplies. (See next chapter.)

12.3.4 Physiological Test of the OCA

The greater part of the physiological testing of the OCA has been carried out on one or two individuals under conditions in which the oxygen flow to the economizer could be regulated. The tests included measurements of arterial oxygen saturation (oximeter) and inspired oxygen fraction as a function of work rate (bicycle ergometer), respiratory minute volume and oxygen flow from the candle at various altitudes and temperatures.[33] A number of physiological and practical tests have been conducted since this detailed analysis, principally with the early water-cooled model of the OCA containing pressed candles and phosphorus ignition.

Use of the OCA for the Resuscitation of Unconscious Personnel at Altitude

In four experiments the OCA has been used to revive persons rendered unconscious from lack of oxygen in the altitude chamber. The results of one of these experiments are shown in Figure 22. It is seen that a candle flow of 4.05 l per min STPD was adequate to resuscitate the unconscious individual at 30,000 ft.

Use of the OCA with Mask Leaks

In contrast to ordinary demand regulators, the OCA affords considerable protection against anoxia resulting from mask leaks. This is illustrated in the experiment of Table 5.

Table 5. Protection against mask leaks. Subject: G.A.M. engaged in light physical activity; Mask A-12 with orifice leak in microphone port; OCA water-cooled model, pressed candle, phosphorus ignition.

Altitude	Oxygen supply	Orifice diameter	Arterial saturation (oximeter)
25,000	Pioneer demand	0.38	Less than 70
30,000	OCA	0.56	97
30,000	Pioneer demand	0.25	Less than 70
30,000	OCA	0.56	100

This characteristic of the OCA is a great advantage to its use in emergencies where mask leaks are likely to be present.

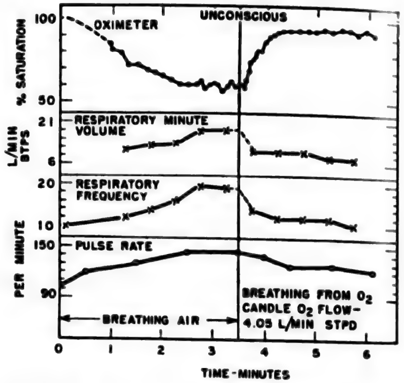


Figure 22. Use of the oxygen candle apparatus (OCA) to revive unconscious personnel at altitude. "Pass-out" experiment at 30,000 ft.

Practical Test of OCA with Untrained Subject in Simulated Emergency

Three men with no previous knowledge of the OCA were subjected to a simulated altitude of 30,000 ft at a temperature of −50 C. The men were given a 3-minute talk on the use of the OCA (water-cooled model, pressed candle, phosphorus ignition). Each man was issued a unit and two spare units were available in the chamber. Each man was given a task to perform while breathing from standard demand equipment. The oxygen supplying their regulators was cut off gradually without their knowledge.

Subject *A* became anoxic from a mask leak and attempted to transfer to his OCA; he was unable to complete the transfer before becoming unconscious. Subjects *B* and *C* were busily engaged in the tasks allotted them and did not notice *A*'s plight. After waiting approximately ½ minute an observer ignited an OCA and fitted it to the unconscious man who recovered completely in a few seconds.

Subject *B* then noticed an increased resistance to breathing (caused by the unknown lowering of his regulator supply) and successfully transferred to his OCA. This subject had never before been in an altitude chamber and was unfamiliar with all oxygen equipment.

Subject *C* likewise noticed the increased resistance to breathing and successfully transferred to his OCA. The candle in this unit had been prepared so that it would go out unexpectedly after four minutes of operation and no flow indicator was provided. The candle was broken and a ring of brass and asbestos inserted in the break. After five minutes the subject became anoxic and started coughing as a result of fumes from the hot asbestos. Subject *A*, who was using the same unit that had revived him 13 minutes earlier, ignited a spare OCA and fitted it to Subject *C*. Ten minutes later the chamber was brought to sea level, all subjects remaining on their OCA units.

12.3.5 Potential Use of Chlorate Oxygen in Aircraft

Suggested Further Developments

Modification of Present OCA for Use or Individual, Portable Oxygen Supply in Transport Planes at Moderate Altitudes. As discussed in Section 12.3.3 and Table 4, much of the potential efficiency of chlorate oxygen is sacrificed in the present form of the OCA in order to allow its operation with demand masks under extreme conditions of altitude, physiological activity, and low temperature. We now consider how the efficiency may be increased for applications involving less stringent conditions.

It is evident from Table 6 that the weight and size of the present OCA could be halved for moderate conditions of altitude, physiological activity, and low temperature.

Table 6. Modified design characteristics of OCA for use at moderate altitudes with A-9 mask.

Maximum operating altitude	28,000 ft
Max resp min vol for equivalent altitude of 5,000 ft at operational altitude of 28,000 ft and −20 C	25 l/min BTPS
Mask, constant flow with self-contained economizer and rebreather bag	A-8
Properties of candle	
Diameter	3.1 cm, 1.2 in.
Length	25.4 cm, 10 in.
Composition	82-7-4-7
Oxygen flow, −20–25 C	3.2-3.8 l/min
Duration, −20,–25 C	30 to 36 min
Total volume of equipment (approx)	024 cu ft
Total weight of equipment (approx)	2 lb
Overall efficiency	
Man-min per cu ft	1250-1500
Man-min per lb	15-18

Chlorate Oxygen to Supply Several Persons at Moderate Altitudes. Semi-Portable Equipment. A slight further increase in overall efficiency may be obtained from chlorate oxygen in apparatus designed to supply several persons simultaneously. Such apparatus could be employed in aircraft which ordinarily have no oxygen installations although it would not be portable in the sense of the individual supply. Table 7 shows the expected characteristics of a chlorate system designed to supply 5 persons for 70 to 80 min at moderate altitudes.

Table 7. Chlorate oxygen installation 5 persons moderate altitude.

Max operating altitude	28,000 ft
Max resp min vol for equivalent altitude of 5,000 ft at operational altitude of 28,000 ft and −20 C	25 l/min BTPS
Masks, constant flow with self-contained economizer and rebreather bag	A-8
Properties of candle	
Diameter	7.6 cm, 3 in.
Length	51 cm, 20 in.
Composition	81-8-4-7
Oxygen flow, −20, 25 C	15-19 l/min STPD 3.0-3.8 l/min per man
Duration, −20, −25 C	72-90 min
Total volume of equipment (estimated)	0.25 cu ft
Total weight of equipment (estimated)	18 lb
Overall efficiency	
Man-min per cu ft	1400-1700
Man-min per lb	20-25

On the Design of Bail-out Equipment. It is evident from a consideration of Figure 19 that the flow rate from chlorate candles may be varied as a function of time to give a variety of flow patterns by suitable adjustment of the ignition system and candle diameter. The weight of candle required to duplicate the flow pattern of the H-2 cylinder is 8 oz and its volume is approximately 0.04 cu ft. It is therefore probable that a chlorate bail-out oxygen unit could be constructed which would be less than one-half the weight and volume of present equipment.

Use of Chlorate Oxygen for Medical Therapy. It was proposed to prepare chlorate candles of a suitable size to generate about 25 l of oxygen per min for a period of 1 hr, to encase these candles in sealed light metal containers provided with smoke filters, Hopcalite, and igniter mechanism. A rack would hold one or more of these units and provide cooling coils, humidifier, and connection to an oxygen distributing

line to patients in a ward or field treatment tent. In operation, a number of units providing the desired oxygen flow would be ignited and inserted in the rack; an attendant would replace spent units with fresh ones once an hour. Units of suitable rate and duration could be supplied for specific uses. The apparatus is simple and compact, and the chlorate units would be lighter and more compact than cylinders containing an equivalent amount of compressed oxygen.

Chapter 13

LIQUID OXYGEN VAPORIZERS FOR AERONAUTICAL, MEDICAL AND ENGINEERING USES

By *S. S. Prentiss*[a]

13.1 INTRODUCTION

Unlike carbon dioxide and some hydrocarbon gases, oxygen gas cannot be compressed to a liquid at normal ambient temperatures. At normal temperatures, oxygen behaves as a noncondensable gas so that the advantages of high density (small volume) can be attained only at the expense of high pressures. On the other hand the great density of liquid oxygen can be obtained only at very low temperatures (−148 C at 1 atm pressure) by the use of the highest order of thermal insulators (nonradiating vacuum jackets) if the storage period is to be useful.

The use of liquid oxygen as a source of oxygen for aviation and medical breathing requirements, engineering uses, with on-the-spot conversion to gas, involves a number of factors representing, in the aggregate, a complex problem which has not been readily solvable in connection with military problems during the war.[23] As a result, the development of oxygen vaporizing equipment,[b] although not difficult from an engineering point of view, has made slow progress because the desire of the military for such apparatus has blown alternatively hot and cold over recent years.

Some of the factors may be mentioned as illustrative of this problem.[14,18,19] The availability of liquid oxygen has very recently improved to the point that serious consideration could be given to its use at advance bases and combat areas. Small, portable liquid oxygen producing plants have been developed which can be moved into, and operated at, forward areas. Liquid oxygen has been available in quantity for a number of years in industrial areas of the United States and suitable equipment for storage and transportation is available.[21] The remarkable advantage of small, light weight liquid oxygen equipment over compressed gas equipment of comparable capacity is of greatest significance aboard aircraft, but the requirements for aircraft oxygen systems have not remained constant with regard either to capacity or rate of delivery. Aircraft not regularly functioning at higher altitudes and aircraft carrying one or two crew members only, require so little oxygen that advantages of liquid oxygen system over gaseous oxygen systems are insignificant while the difficulties are magnified. However, as aircraft requiring larger crews were regularly operating at higher altitudes and the cruising range was increased, the necessity for carrying large quantities of oxygen again called attention to the advantages of liquid oxygen. These factors did not culminate in an all-out effort to produce liquid oxygen installations for military aircraft until the last year of the war.

Other delaying factors should be mentioned, namely, a great advance in the recognition of physiological requirements for oxygen and the development of improved dispensing equipment such as demand regulators and oxygen masks, requiring constant modification of the oxygen supply system. Again this was not too difficult from the engineering point of view but the constant changes in specifications for the oxygen vaporizer hampered the construction of experimental units.

13.2 PROPERTIES OF OXYGEN[26]

The variation of the boiling point and vapor pressure of liquid oxygen with absolute pressure is given in Figure 1.

The latent heat of vaporization at the boiling point is equal to 50.8 cal per g or 91.51 Btu per lb. The latent energy required to vaporize liquid oxygen at the boiling point and raise the temperature of the gas to 20 C is approximately 88 cal per g or 160 Btu per lb. This is equivalent to 4 kwh per 1,000 cu ft of oxygen.

The specific heat of the gas (C_p) is equal to 0.218 cal per g C. The specific heat of liquid oxygen at −200 C is equal to 0.393 cal per g C.

[a] Technical Aide, Division 11, NDRC.

[b] Apparatus for converting liquid oxygen to gaseous oxygen under controlled conditions has been variously designated liquid oxygen vaporizers, liquid oxygen converters. Apparatus of chief concern in this chapter relates to vaporizers or converters for supplying gaseous oxygen at relatively low useful pressures, on a demand basis, to a using device such as breathing equipment, and cutting and welding torches, at a relatively low operating pressure. Apparatus for vaporizing liquid oxygen for the purpose of charging compressed gas cylinders at high pressures is touched upon briefly.

The specific gravity of liquid oxygen at 1 atm is 1.14 and this decreases approximately 14% at a pressure of 100 psi and 30% at a pressure of 400 psi. One liter of liquid oxygen at atmospheric pressure produces approximately 800 l of gaseous oxygen at 20 C and 1 atm pressure.

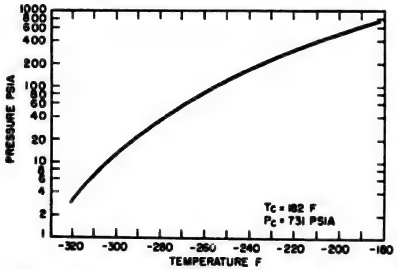


FIGURE 1. Effect of vapor pressure on boiling point of liquid oxygen. Note: TC in zero degrees Farenheit (−182 F).

It will be apparent that the energy requirements of a vaporizer will vary considerably with the pressure range over which the vaporizer is operated. For example, starting with 25 l of liquid oxygen at 1 atm absolute pressure, it will be necessary to supply 225 kcal to warm this body of liquid to a temperature at which the boiling point is equivalent to 5 atm abs, or an operating gauge pressure of 60 psi.

13.3 TYPES OF LIQUID OXYGEN VAPORIZERS

Based upon different principles of operation, six types of liquid oxygen vaporizers are suitable for aviation and other military purposes. Division 11 of NDRC has contributed improvements to four of these types and these will be discussed in detail below.

Type 1. Liquid oxygen is held under operating pressure in a container with suitable thermal insulation and withdrawn therefrom through a length of metallic tubing with sufficient exposure to the atmosphere to evaporate the liquid oxygen and warm the resulting gas. This is the simplest form of apparatus which might be used for the purpose and is basic to some of the following types in which refinements are added to control carefully the operating pressure. An example of such vaporizers is that produced at the University of California[2] for the operation of cutting and welding torches. An alternative form of the apparatus has the liquid oxygen container at atmospheric pressure from which liquid oxygen is delivered by means of a pump through vaporizing and warming coils[13] (see Chapter 6).

Type 2. A small, poorly insulated reservoir provided with atmospheric vaporizing coil and automatic pressure controls is connected to a larger well-insulated reservoir from which it is charged at frequent intervals during operation. Early apparatus developed by Akerman at the University of Minnesota was of this type.[3,7,24]

Type 3. Atmospheric vaporizing coils and automatic pressure controls are combined directly with a well-insulated reservoir in which the entire charge of liquid oxygen can be stored for appreciable lengths of time. Later models of the Akerman vaporizer, constructed upon metal Dewar containers, are of this type.[6,25]

Type 4. Liquid oxygen, at a temperature corresponding to a boiling point less than the desired operating pressure, is contained in a vessel equipped with means for subjecting the *gas phase* to additional pressure until the desired operating pressure is obtained. Preferably the gas phase is pressurized by the evaporation of a small amount of liquid withdrawn from the container. The heat requirement for pressurizing this type of vaporizer from liquid, initially at atmospheric pressure, is considerably less than that required when the whole body of the liquid must be raised to a boiling point equivalent to the operating pressure. This type is represented by vaporizers by Piccard[3] and Wildhack.[20]

Type 5. Liquid oxygen is contained in a well-insulated container such as a Dewar flask equipped with electric heating coils in the liquid phase. The electric heating circuit is provided with automatic pressure controls and serves to pressurize the apparatus when the liquid oxygen is initially at atmospheric pressure and also to vaporize and deliver gaseous oxygen therefrom. Such vaporizers have been developed by Mathis and Milan[10] and Linde Air Products Company.[12] In a refinement developed by Arthur D. Little, Inc., the liquid oxygen is absorbed in a mass of fine glass fiber in which is embedded the electric heating element; liquid oxygen so confined will not spill and operation is independent of position.

Type 6. Pressure control and part of the heat of vaporization is furnished by an electrical system to which is added vaporizing coils warmed by the ambient atmosphere. Such a combination vaporizer has been developed at the University of Toronto.[15]

Inasmuch as Division 11 has made no contribution to types 5 and 6, they will not be further discussed in this report. It should be noted, however, that the electric energy required for pressurizing the equipment in a short time and for maintaining oxygen delivery (5 w per l per min STP) required on aircraft, constitutes an appreciable drain upon the electrical facilities of the aircraft and for this reason the development of vaporizers depending entirely upon ambient heat appeared desirable.

13.3.1 Note on Use of Liquid Oxygen Vaporizers Developed by Division 11

The most stringent requirement for liquid oxygen vaporizers has been in the field of aircraft installations and for this reason the principal effort has been in this direction. It is felt that the vaporizers developed for this use will be directly useful also in the field of therapeutic administration of oxygen in hospitals, although some of the controls will not be required. Although the aircraft units will operate cutting and welding torches in the field satisfactorily they have not been constructed with sufficient strength and ruggedness to withstand this usage. Emphasis on low weight is not present in field engineering apparatus and it may be that the presently developed units will be suitable for this use when provided with protective casings. Large units for permanent aircraft installations do not have the severe conditions of operations placed upon them that occur when the corresponding unit is to be used as a small or portable model for walk-around service and, therefore, the development of such portable units constitutes a special problem.

13.4 TYPE 1—GIAUQUE LIQUID OXYGEN VAPORIZER

A simple form of liquid oxygen vaporizer suitable for the operation of cutting and welding torches, oxygen therapy, and perhaps also for oxygen supply on aircraft (within limits) is shown in Figure 2. The vaporizer apparatus shown on the left of the figure is attached to the vacuum-jacketed Dewar container shown on the right of the figure by means of a screw fitting soldered to the neck of the container. This vaporizer consists of a tube of stainless steel or other material of low heat conductivity which dips to the bottom of the liquid in the container, a gas-tight connection for the vapor phase above the liquid in the container, an external coil of tubing connected directly to the dip tube extending to the bottom of the container, and pressure gauge and safety valve connecting to the gas phase. The container may be pressurized in a number of ways; for example (1) by pulling oxygen from a cylinder through the liquid until the temperature of the liquid is raised to the

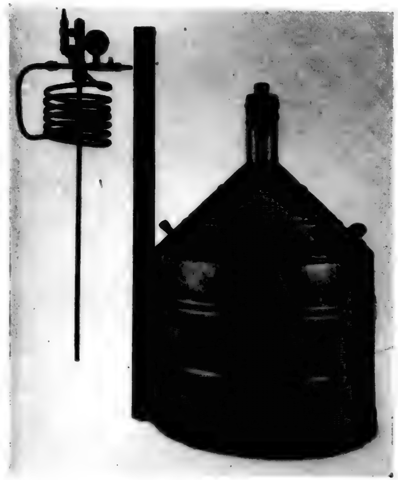


FIGURE 2. Liquid oxygen vaporizer.

desired boiling point, (2) by allowing the container to stand until the liquid is warmed by natural heat leak or accelerated by laying the container upon its side, whereby heat is rapidly introduced through the neck of the container, or (3) by introducing dry gas directly into the gas phase above the liquid. After pressurizing, gas may be withdrawn from the external end of the evaporator tubing through a suitable needle valve or reducing valve. During such withdrawal, liquid oxygen enters the vaporizing tubing and is vaporized and warmed therein. Vaporization and withdrawal of oxygen, therefore, occurs automatically upon a "demand" basis. The pressure within the container is limited by suitable adjustment of the safety valve. The effectiveness of the vapor-

izer tubing may be enhanced by the insertion of a twisted strip of brass to serve as a turbulator.

The following information applies to the apparatus illustrated in Figure 2. The coil shown consists of 12 ft of 3/8-in. copper tubing with a turbulator strip 0.255 in. wide and 0.033 in. thick, twisted 5 turns per ft and pulled through the 3/8-in. tube before it was coiled.

A needle valve, shown with the vertical hose connection attached, is used to control the rate of gas flow. The horizontal needle valve is provided for pressurizing the gas phase of the container from an external source of dry gas under pressure.

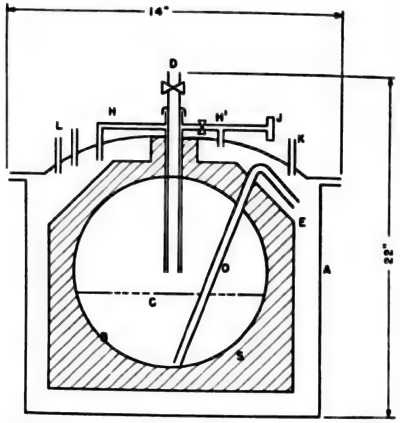
The 50-l container will supply 1,500 cu ft of oxygen gas STP per filling. The vaporizer is designed to deliver 1 cfm of oxygen warmed to ordinary temperature, which amount is sufficient to enable an oxyacetylene torch to cut 3/4-in. steel plate at the rate of 1 ft per min. If greater rates of flow are desired, vaporizer tubing may be increased in length and/or diameter.

There is little tendency for liquid convection when compressed air or other gas is admitted over liquid oxygen as the equilibrium liquid at the surface would be less dense by about 0.2 g per ml.

13.5 TYPE 2—EARLY AKERMAN LIQUID OXYGEN VAPORIZER[c]

Refinements of the apparatus just described appeared to be necessary for aircraft use. These refinements provided for operation at constant absolute pressure and a certain degree of economy when the apparatus stands for long periods of disuse.

The principles of operation of the vaporizer are shown in Figure 3 and the apparatus in Figure 4. Liquid oxygen is contained in a thin-walled metallic container B surrounded by thermal insulations which in turn is encased in a vessel A capable of withstanding the operating pressure of the system. There is a small space provided between the inner, thermally insulated container and the outer pressure casing. Tube O connects the liquid phase in the inner container with this space between the containers. When the system is under pressure and the pressure is equalized between the inner container and the outer container, no liquid will flow through the tube. However, if gas is withdrawn from the outer container, thus lowering the pressure slightly, liquid will be caused to flow through tube O into the space between containers E, where it will be rapidly vaporized through heat transfer with the outer container. The rate of evaporation, for continuous operation, is limited by the heat transfer between the outer casing and the ambient atmosphere.



B SILVER BOTTLE (15 LITER)
S INSULATION
A CAST ALUMINUM PRESSURE VESSEL
O SPILLING TUBE
L PRESSURE POP-OFFS
J PRESSURE GAUGE
H PRESSURE OPENED BY-PASS
H' MANUALLY OPENED BY-PASS (PETCOCK #1)
K OUTLET THROUGH FILTERS TO DEMAND SYSTEM
C BAFFLE PLATE
D FILLING TUBE

FIGURE 3. Akerman liquid oxygen converter.

A pressure-opened by-pass valve H connects the gas phase C directly over the liquid with the vaporization chamber E between the inner and outer containers. When this by-pass valve is open, the pressure between the inner liquid container and the vaporization chamber is, at all times, equalized and no liquid will be transferred to the vaporization chamber. Instead, the liquid C will be vaporized when gas is withdrawn and the temperature, and hence the pressure, will be gradually lowered. In operation, the pressure-opened by-pass valve H is adjusted to open and close at the minimum operating pressure desired in the system. If the pressure in the system is initially above this minimum pressure and gas is withdrawn, the pressure will gradually fall

[c] An early form of this apparatus[24] was developed by the University of Minnesota. Subsequently an NDRC contract was arranged with the University of Minnesota in order that the development might be better adapted to flight requirements as specified by the Navy Bureau of Aeronautics.

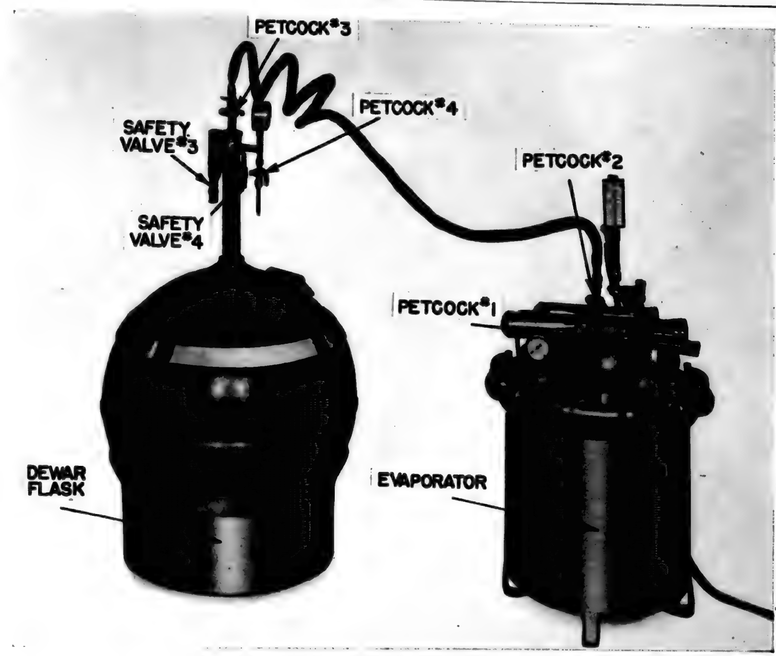


FIGURE 4. Photograph of Akerman liquid oxygen converter.

until the minimum pressure is reached, whereupon the by-pass valve will close and further withdrawal will cause transfer of liquid to the vaporizing chamber.

The apparatus is provided with suitable connections and vents D, H, K for filling with liquid oxygen and a dual set of safety valves L. The vaporized oxygen is caused to pass through a suitable filter for the removal of odorous impurities. A large storage reservoir (a standard 50-l Dewar container) is provided in which the liquid is contained at a pressure in the neighborhood of operating pressure.

The experimental model of the vaporizer weighs 42 lb empty and can be charged with 15 l, or 34 lb, of liquid oxygen. The outer container is of aluminum. The inner container has a thin-walled silver sphere surrounded with rock wool insulation.

The safety valves were adjusted to pop at about 75 to 80 psi and the pressure-controlled by-pass valve was set at 45 psi. Therefore, the maximum pressure attained on standing is 75 to 80 lb and the minimum operating pressure is 45 lb. The vaporizer maintains a flow of approximately 100 l of oxygen gas per minute STP continuously, or higher rate of flow for short periods of time. Heat leak through the thermal insulation is sufficient to vaporize approximately 10 l of oxygen STP per min. When charged with liquid oxygen at ambient pressure and allowed to stand, this heat leak is sufficient under normal conditions to raise the pressure to 45 psi gauge in 17 to 20 min or to the pop-off pressure in 35 to 45 min. This rate of evaporation loss is, in general, too high for storage purposes and, therefore, the main body of the liquid oxygen should be stored in the Dewar reservoir in which evaporation losses run from 3% to 5% in 24 hr.

A feature of this apparatus is the pressure-control by-pass valve which was constructed with an evacuated sylphon control element providing maintenance of constant absolute minimum operating pressure at all altitudes. This was originally thought desirable but in the event that it is more advantageous to maintain constant gauge pressure, a by-pass control valve could be substituted which maintains a constant differential with the ambient pressure.

Several schemes were proposed for causing this apparatus to operate satisfactorily in an inverted position for long periods of time.[3] The simplest arrangement to attain this end is to make all connections to the gas phase in the liquid oxygen container to a tube which opens in the center of the spherical container and to arrange that this container is at all times a little less than half full of liquid.

13.6 TYPE 3—IMPROVED AKERMAN VAPORIZER

13.6.1 Description

The vaporizer just described had the disadvantages of (1) unnecessary weight, (2) high evaporation losses, and (3) complicated construction unsuited to production.

Several later models were developed in which a standard spherical Dewar container was equipped with a vaporizing chamber in the form of a double-walled cylinder. The control features of pressure-operated by-pass valve, syphon tube for transfer of liquid oxygen, safety valves, etc., were retained. One of these vaporizers of 5-l capacity is shown in Figure 5 and a diagrammatic sketch in Figure 6. The operation of this model is similar to type 2. In Figure 6, liquid oxygen *C* in container *A-B* passes through the central tube and valve *F* to the ring-shaped evaporating chamber *E* when gas is withdrawn at *K*. When the pressure in the system exceeds normal operating pressure, pressure-controlled by-pass valve *H* opens, equalizing the pressure between the gas and liquid phases preventing further discharge of liquid to *E* until the pressure again falls to normal operating valve. Valves *D*, *F* and *G* are useful when the container is filled with liquid. A small container *I* may be filled with liquid oxygen, which, on vaporizing, assists in pressurizing the apparatus. In later models, *I* is arranged to discharge liquid directly into the vaporizing chamber (coils) so that the additional heat transfer surface may be utilized. *J* is a pressure gauge, *L* a safety valve.

In a still further improvement, a coil of tubing was substituted for the double-walled vaporizer and the tubing, control regulators, safety valves and all other apparatus were compactly arranged around the neck of a standard Dewar container of 25-l capacity. This apparatus is illustrated in Figures 7 and 8.

When a Dewar container was used, the heat leak into the liquid oxygen was so small that several days were required to attain operating pressure on normal standing. This time could be greatly decreased by inverting the apparatus and thus introducing heat through the neck of the flask. However, the best method consisted in bubbling oxygen gas directly into the liquid. This oxygen gas could be obtained from an external source such as a cylinder of compressed gas or a small portion of liquid could be withdrawn from the apparatus into an auxiliary reservoir, vaporized and warmed in the main evaporator coils and then returned to the main body of the liquid. By such a procedure enough heat could be transferred in a few minutes to raise the vapor pressure of the liquid to 50 or 60 psi.

13.6.2 Operation of Type 3 Vaporizers

The vaporizer shown in Figure 5 was tested under various conditions including installation in the altitude chamber of the Johnson Foundation, in both the warm and the cold.[11] The results of these tests under simulated flight conditions with a number of subjects is summarized in Table 1; the experimental set-up is illustrated in Figure 9.

Physical characteristics of the model shown in Figures 7 and 8 exclusive of the portable unit are:

Height, overall	29 in.
Outside diameter	19 in.
Weight, empty	60 lb
Weight, full	120 lb
Weight of liquid oxygen	60 lb
Length of vaporizing coil	50 ft
Operating pressure	52 psi

The following performance tests were obtained with this model.

The converter was filled in 13 min from a warm state through a $^3/_8$-in. diameter tube from a storage tank pressurized at 10 psi. With the storage tank pressurized at 20 psi and with the converter cold the filling process required 6 min.

Inasmuch as this model had not been equipped with self-pressurizing apparatus, an operating pressure was produced by bubbling gaseous oxygen under pressure through the liquid phase. When an equilibrium pressure of 52 psi was reached, the pressure remained constant, regardless of flow conditions, until the liquid oxygen supply was exhausted.

The flow was maintained at 100 l per min for 1 hr. The temperature of the oxygen at the coil outlet decreased slowly until at the end of the hour it was 30 below the ambient temperature of 70 F. At the end of the hour the flow was suddenly increased to 400 l per min, ambient, whereupon the temperature of the oxygen at the coil outlet dropped to —100 F in 1.25 min.

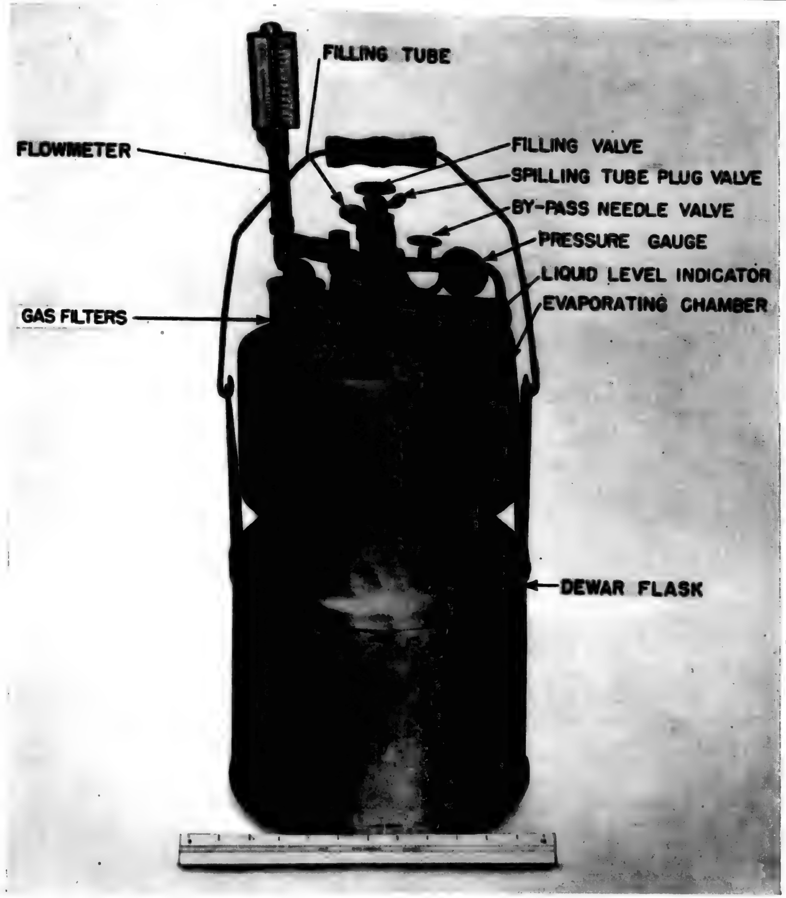


FIGURE 5. Five-liter vaporizer.

TABLE 1. Test results of 5-liter vaporizer.

Ambient temp C	Time period min	Altitude feet	No. of subjects	Auto-mix	Work condition	O_2 consumption oz	Line pressure psi	Gas temp at flowmeter C	O_2 liters STPD	O_2 liters ATPD	O_2 liters BTPS	Average flow rate l/min STPD	Average flow rate l/min ATPD	Average minute volume per subject BTPS
22	6.5	SL	7	Off	Exercise	56	43–47	..	1060	1130	1290	163	172	28.[illegible]
	5	SL	7	Off	Rest	14	45–48	..	276	295	336	55	59	9.[illegible]
	5	20,000	7	Off	Exercise	22	41–44	6	436	1040	1250	87	208	35.6
	5	20,000	7	Off	Rest	8	43–44	11	158	367	454	32	73	13.0
	5	20,000	7	On	Exercise	13	42–44	..	256	600	734	51	120	21.0
	..	20,000	7	Off	....	..	42–47	(deep breathing in unison)			..	..	..	..
	5.5	28,000	7	Off	Rest	4	47	11.5	79	259	341	14	47	8.9
	5	28,000	7	Off	Exercise	11	46–48	11	218	719	940	44	144	26.8
	..	28,000	7	Off	....	..	46–47	(deep breathing in unison)			..	..	..	..
	5	35,000	6	Off	Rest	3	48.5	12	60	272	394	12	54	13.1
	5	35,000	6	Off	Exercise	10	47–48	13	198	900	1300	40	180	43.3
−40	5.5	SL	8	Off	Rest*	25	43–46	..	496	425	602	90	77	13.7
	5	20,000	7	Off	Rest*	9	53–54	..	178	332	510	36	66	14.6
	5	20,000	6	Off	Exercise	22	52–54	..	435	812	1230	87	162	41.0
	10.5	27,000	7	Off	Rest*	16	53–54	..	317	796	1285	30	76	17.5
	5	27,000	7	Off	Exercise	17	52–53	..	337	848	1368	67	170	39.0
	5	35,000	7	Off	Exercise	13	53–54	..	258	940	1700	52	188	48.5

* Subjects did not remain quiet during rest periods because of insufficiently heated clothing.

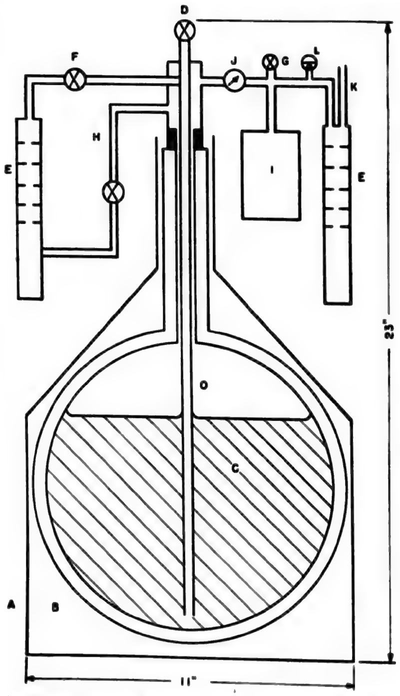


FIGURE 6. Revised Akerman liquid oxygen evaporator.

A converter was then mounted at an angle of 60 degrees from the vertical and the test just described was repeated with similar results.

FIGURE 7. 25-liter vaporizer.

FIGURE 8. Details of 25-liter vaporizer.

The converter was inverted, the flow of oxygen was maintained at 100 l per min ambient for a period of 6 min. At the end of 6 min the temperature of the gas at the coil outlet was within 10 F of the ambient temperature. When the flow was increased to 400 l per min ambient, the temperature of the exit gas dropped approximately 30 F in 3 min.

The converter was next tested at a temperature of −55 F with results quite similar to those obtained at room temperature with the exception that a flow of 400 l per min caused the temperature at the coil outlet to fall almost immediately to a temperature of −100 F, the limit of the measuring instrument.

Tests conducted with the converter in an atmosphere at 100 F and 95% relative humidity gave results very similar to those obtained at normal ambient condition.

After completion of performance tests, the converter was subjected to acceleration test of 9 g with a 32-lb load of liquid oxygen; a second acceleration test to 9 g with a 60-lb load of liquid oxygen; a 25-hr vibration test at a displacement of 0.025 in. and at a frequency cycling from 6 to 42 cycles per second, once every minute with converter empty; a similar test with converter containing 31 to 37 lb of liquid oxygen; a sloshing test with converter containing 60 lb of liquid oxygen and rocking about 7 degrees from the vertical, from one side to the other, once every cycle at a rate of 35 cycles per min for 110 min; and a third acceleration test to 9 g with 60 lb of liquid oxygen in the converter. Vaporization losses were measured over night during this test procedure; no significant changes were observed.

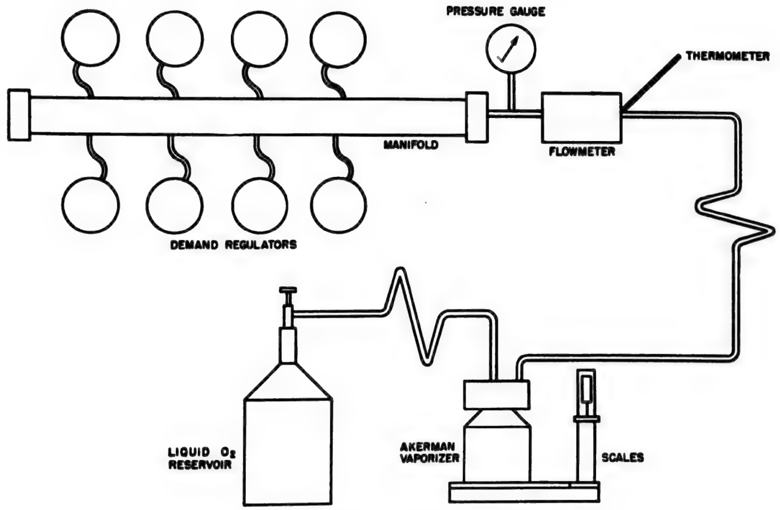


FIGURE 9. Flow sheet of Akerman vaporizer.

After the aforementioned tests were made the vaporizer was modified by the removal of the filter and the substitution of a small reservoir of 1-l capacity in place of the filter, with suitable connections to permit its use in the build-up of the initial operating pressure according to the following procedure. The reservoir is provided at the top with a connection to the liquid oxygen spill tube through a two-way valve which alternately connects the liquid oxygen spill tube to the bottom of the vaporizing coil for normal operation. The bottom of the auxiliary reservoir connects through a valve to the top of the vaporizing coil. The auxiliary reservoir also has a valve which vents directly to the atmosphere. In operation the converter is filled with liquid oxygen in such a manner that a pressure of at least 2 or 3 psi is present. The two-way valve is then adjusted to connect the liquid oxygen in the Dewar container with the auxiliary reservoir and the vent valve to the atmosphere is opened. The initial pressure in the converter will then force the liquid over into the auxiliary reservoir until the latter is filled, whereupon the vent valve to the atmosphere is closed, the two-way valve readjusted to connect the liquid oxygen tube with the bottom of the vaporizing coil, and the valve between the bottom of the auxiliary reservoir on the top of the vaporizing coil is opened. Liquid oxygen from the auxiliary reservoir is thereupon forced into the vaporizing coil, where it is vaporized and warmed to approximately ambient temperature. It then passes into the main body of liquid oxygen in the Dewar container where it is condensed, thus warming and raising the pressure within the system. This process may be repeated until the desired operating pressure is obtained. In operation, each cycle required approximately 5 min and raised the pressure of the system 20 psi when there was no draft other than convection. Hence, an operating pressure of 60 to 65 lb could be obtained with 3 cycles in 15 min. If a breeze was caused to blow upon the apparatus, as from a small fan, two cycles were sufficient to raise the pressure to 57 psi in a total elapsed time of 11 min.

Still other changes were made. Another layer of evaporating coil was added, increasing the length to approximately 80 ft, thus increasing the evaporative rate approximately 50%. The auxiliary reservoir for pressure build-up was connected into the converter system with check valves so that the only operation to be performed during pressure build-up is the opening and closing of the atmospheric vent valve; this simplifies the pressure build-up operation, further reducing the time required for obtaining operating pressure and furthermore making it possible to increase operating pressure even while the converter is in use.

13.7 TYPE 4—GAS PHASE PRESSURIZED LIQUID OXYGEN VAPORIZER

In the vaporizers described so far, the gas pressure in the system is obtained by raising the boiling point of the liquid phase to the desired operating pressure. This necessitated the introduction of a relatively large amount of heat to increase the boiling point from atmospheric pressure to a desired operating pressure in the neighborhood of 65 psi. The introduction of this large amount of heat can be avoided if a small portion of the liquid is vaporized to gas and introduced in the gas phase above the liquid. In practice, a thin layer of liquid at the surface can be warmed to the desired boiling point and remain distinct from the main body of the liquid because of a considerable decrease in density with increased temperature. Little experience has been achieved on the effect of vibration and sloshing, or other action on the destruction of this warm layer.

The operation of a successful system employing this principle depends upon the gravity feed of liquid to a vaporizing coil. A system[c] wherein a standard Dewar container is utilized in the inverted position, neck down, is illustrated in Figure 7. Further modification[d] utilizes a special Dewar container provided with a liquid drain connection in the form of a low thermally conducting spiral tube within the vacuum housing. This system is illustrated diagrammatically in Figure 10 and the apparatus is pictured in Figures 11 and 12.

Referring to Figure 10, a Dewar flask, B, is filled with liquid oxygen at approximately atmospheric pressure. When valve F is opened, the following action takes place to pressurize the system automatically to the desired operating pressure. Liquid flows from the bottom of container B into pressure evaporator coil N where it is vaporized and the gaseous oxygen is further warmed by a continuation of the coil N in the upper part of the apparatus. The warmed oxygen is then passed into the container B above the liquid C where a small portion is recondensed on the surface of the liquid, thus producing a warm layer. Within a short period of time, this warm upper layer reaches a temperature at which the boiling point is equal to the desired operating pressure, whereupon a pressure-controlled valve H closes, preventing further flow and evaporation of liquid. When the system is under operating pressure, valve K may be opened, whereupon liquid flows from the bottom of the flask B into a check valve to the main evaporator coil where it is then vaporized and warmed to approximately ambient temperature.

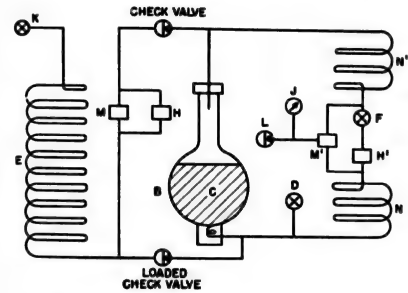


FIGURE 10. Diagram of type 4 gas phase oxygen vaporizer.

If, however, the pressure in the system greatly exceeds the set operating pressure, a pressure controlled by-pass valve H will open, permitting withdrawal of gaseous oxygen from the container B, until the pressure of the system falls to the desired operating pressure. This operating pressure is determined by the setting of the pressure-controlled valves H and H'.

The operation of this automatic pressurizing system is dependent first upon adequate flow of liquid oxygen through the pressurizing circuit under the low hydrostatic head of the liquid oxygen in container B and, secondly, upon the maintenance of a relatively thin warm layer of liquid oxygen to prevent condensation of oxygen in excess of that supplied by the pressure evaporator system.

The apparatus, as constructed, is designed to operate in the normally upright position and in an inverted position. To provide for the inverted operation, the pressurizing coil is made in two parts, N and N', so that one or the other will operate with the hydrostatic head of liquid in one or the other positions. The safety valve L and the connection to the main evaporator coil are controlled by gravity-operated valves M and M' in order that the functional parts of the system will be properly connected to the liquid or gas phase. For example, in the upright position, gravity-operated valve M' connects pressure relief valve L and pressure gauge J to the neck of container B (gas phase). In this position, gravity-operated valve M is closed so that withdrawal of gas

FIGURE 11. Type 4 gas phase oxygen vaporizer.

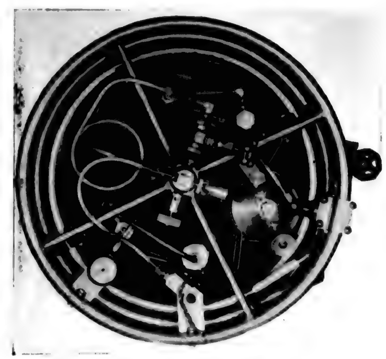


FIGURE 12. Details of type 4 gas phase oxygen vaporizer.

[d] Experimental models were constructed and tested by W. A. Wildhack, National Bureau of Standards. NDRC sponsored a production model,[20] described and illustrated here.

through the main evaporator coil will be determined by the pressure-controlled valve H. Now, when the apparatus is inverted, valve M changes connection of pressure relief valve L to what formerly was the bottom of the container B, but which now connects directly with the gas phase. Valve M is now open in order that liquid may flow directly to the main evaporator coil. During operation in the inverted position, the automatic pressure-control valve H does not function; however, the small evaporation loss is negligible over the periods in which the apparatus will be operated in the inverted position.

In the experimental unit shown in Figures 11 and 12, a pressure buildup apparatus similar to that described for the model immediately preceding, is also included in order to permit experimental evaluation of the two systems.

13.8 PORTABLE OR WALK-AROUND VAPORIZER

In order to provide large aircraft with walk-around units which would not be dependent upon high pressure gas lines for recharging and which furthermore would have a higher oxygen capacity than was generally available, a walk-around unit using liquid oxygen was developed. Two types of apparatus differing somewhat in principle and method of operation were developed.

Type A, shown schematically in Figure 13, includes a Dewar container B of 1-l capacity, measuring approximately 6 in. in diameter and 12 in. high, provided with a closure at the top of the neck through which passes a tube O extending to the bottom. A second connection is made to the gas phase above the liquid C, directly into the closure. Both the gas phase and the liquid phase connections go to a three-way gravity-operated valve M so constructed that a take-off connection from the valve is at all times connected with the gas phase in the container, regardless of whether the flask is in an upright or an inverted position. This valve connects with a length of copper tubing E designed to warm the gas. A diluter demand regulator P, a pressure relief valve L, and a pressure gauge J are connected to the outlet of this warming coil. Filling connections D and G are also provided. In operation the apparatus is inverted, whereupon there is a rapid introduction of heat through the neck of the flask raising the pressure in the system. This pressure persists when the flask is again righted. A standard demand type mask is connected to the regulator at K. As oxygen is withdrawn through the regulator, it is constantly replenished by boiling of the liquid in the container, which in time serves to reduce the pressure in the system. When the pressure is reduced below a certain minimum, as evidenced by resistance to breathing or by falling of the pressure gauge, the apparatus may again be inverted for a short period during which the pressure is again built up. Because of the operation of the three-way gravity valve, it is possible to withdraw oxygen for breathing during this pressure build-up period.

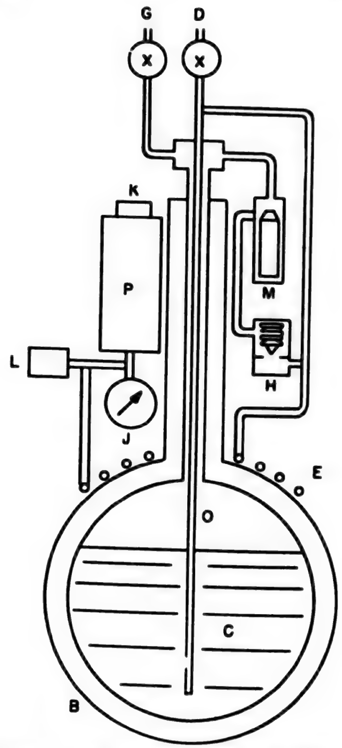


Figure 13. Diagram of portable converter, type A.

Such apparatus, charged with 1 l of liquid oxygen and equipped with standard available regulators operating in the pressure range of 50 psi to 150 psi may be used under normal conditions of diluter operation for a period of 15 to 45 min before it will again be necessary to invert the apparatus for pressuring. If the apparatus is stored for some hours before use, the pressure will slowly increase to the pop-off value and will be immediately available for use when connected.

Experimental apparatus of this type weighs approximately 5 lb empty, can be charged with 2¼ lb of liquid oxygen, which is sufficient to yield 800 l of gas STP.

Type B, a later form of the apparatus, is shown in Figures 14 and 15. The controls and method of operation of this form is quite similar to the 25-l vaporizer described above under type 3. Liquid oxygen is withdrawn through a tube O into a coil E and thence to a diluter demand regulator P. A pressure-controlled by-pass valve H insures operation at a constant pressure. A gravity-operated valve M closes this by-pass when the apparatus is inverted. During periods of operation in the inverted position, gas is withdrawn directly from the gas phase of the liquid and no vaporization of liquid takes place in the evaporator coil, although additional heat is supplied to the liquid through the neck of the container. A pressure relief valve L and pressure gauge J is connected to the withdrawal line serving the diluter demand regulator P and is always in direct connection with the gas phase of the container when the pressure of the system is in excess of the minimum operating pressure.

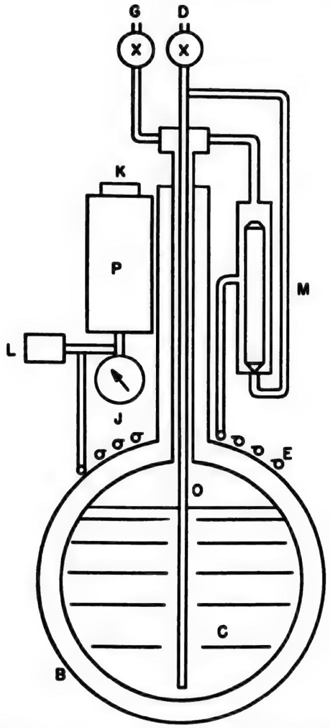


Figure 14. Diagram of portable converter, type B.

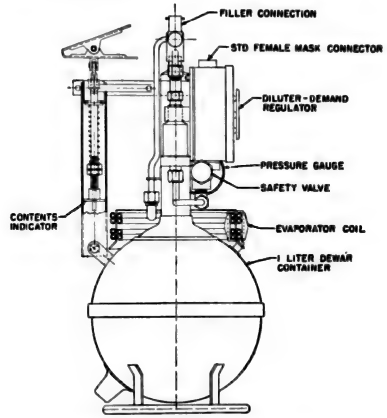


Figure 15. Details of portable converter.

Filling connection D and vent valve G is provided at the top. A carrying handle encloses a spring scale for indicating contents of liquid oxygen.

A one-stage diluter demand regulator operating with a head pressure of between 9 and 25 psi was available in experimental form (The Aro Equipment Corporation, Cleveland, Ohio). In the experimental models produced, the pressure-controlled by-pass was set to open at pressures above 15 psi so that this pressure became the minimum operating pressure. The pressure relief valve was set at 25 to 30 psi.

These valves may be readily altered to suit the operating characteristics of the demand regulator used.

Physical Characteristics	½-Liter Size	1-Liter Size
Height	12.5 in.	14.5 in.
Overall diameter	5.5 in.	6.2 in.
Weight empty	4.9 lb	5.4 lb
Weight full	6.1 lb	7.7 lb
Weight of liquid oxygen	1.2 lb	2.3 lb
Available gaseous oxygen	375 1	764 1 STP
Operating pressure	15 to 17 psi	15 to 17 psi

A vaporization loss in the 1-l size, resulting from heat leak when the converter is not used, is at a rate of 0.915 lb of liquid oxygen or 40% total capacity per 24 hr. Oxygen delivery from the apparatus appeared to be adequate for diluter demand operation although maximum flows at sea level with no dilution tended to freeze the regulator and impair its operation. Approximately 6 ft of $^3/_{16}$-in. copper or aluminum tubing was used for the coil. If greater delivery rates are desired, this coil length and diameter can be increased. The ½-l size is pictured in Figures 7 and 8 as being recharged from the 25-l converter.

Some attention was given to gun-fire hazard of liquid oxygen containers of the spherical Dewar type. Twenty-five-liter containers, when hit squarely by 50 caliber API, exploded or came apart in such a fashion as to scatter large pieces of the container. Preliminary tests indicated that this could be prevented by lacing with steel wire or cable.[19] However, much work still remains to be done in order to estimate the minimum requirements and the hazards of scattering the liquid oxygen contents in the fuselage of a plane.

13.9 RECOMMENDATIONS FOR FUTURE RESEARCH

The models of liquid oxygen vaporizers constructed and reported herein should be given tests under flight conditions to estimate not only their operating characteristics but to gain a clear insight into such apparatus under flight conditions. It is believed that the apparatus might be considerably simplified (in the case of the 25-l size) by removing the requirement for operation in inverted position. Some effort was made to obtain 1-liter containers of stainless steel or aluminum which would be much lighter and stronger than the standard copper containers available. This investigation should be continued as well as a study of modifications of shape and arrangement of apparatus to provide greater compactness. As already pointed out by the Army Air Forces, the use of portable 1-l converters and means for recharging aboard aircraft may result in the elimination of the standard oxygen installation on the larger aircraft, with the elimination of considerable weight of equipment, decreased hazard from gun fire and increased flexibility of operation.

Chapter 14

INSTRUMENTS FOR TESTING OXYGEN

By *S. S. Prentiss*[a]

14.1 INTRODUCTION

In order to meet the requirements for special field testing apparatus and instruments for field equipment, the following instruments were developed.

1. Instrument for determining the partial pressure of oxygen in a mixture of gases.
2. Instrument for determining the moisture-content of gases (2 methods).
3. Instrument for determining a combination of properties of compressed oxygen gas.
4. Thermometer covering a large range of low temperature.
5. A dial-type liquid level gauge.

Considerable need existed for methods of determining the concentration of oxygen in a mixture of gases which would facilitate the rapid analyses of breathing atmospheres, purity of oxygen production, and presence of hazardous concentrations of oxygen in combustible gases. The Pauling oxygen meter, an ingenious device for measuring the paramagnetic properties of gases (amongst which oxygen is unique) proved so successful in determining the partial pressure of oxygen in gas mixtures that a great number of modifications have been developed in order to meet the requirements of specific problems. This instrument has enormously simplified analysis of experimental gas mixtures in the study of breathing and has simplified the construction of warning and indicating devices for submarines, aircraft, and gas generating plants. The apparatus and some of the modifications will be described below.

The moisture content of aviation oxygen is critical at 0.020 mg per 1 STP, or a frost point of −57 C. Oxygen that contains moisture in excess of this value was deemed likely to freeze oxygen equipment on aircraft because of the low temperatures at high altitudes, thus introducing hazards of anoxia. Oxygen, as commercially produced, normally has a moisture content much lower than this critical value; however, it appeared desirable to test every cylinder of compressed oxygen intended for aircraft use, because of the possible presence of water in the cylinder prior to filling.

The National Bureau of Standards developed apparatus for determining, with considerable accuracy and convenience, moisture content of gases by measuring the electrical conductivity of a thin film of phosphoric acid in contact with a gas sample under pressure.[20,21,22] Production models of this instrument were made available by several manufacturers, for example, the American Instrument Company. NDRC undertook to develop apparatus which, though somewhat less accurate, would be more compact, rugged, and more suited in field use, and for a rough and ready determination of moisture content at ambient pressure. The first method devised, based upon induced color change in chemicals of a type related to malachite-green, was very ingenious, but interposed insurmountable difficulties of manufacture, standardization, and storage. As a second approach, apparatus of the dew-point or frost-point type was developed. Both devices will be described in the following text.

Some experience of the Services indicates the desirability of a portable instrument for quickly checking the following properties of compressed cylinder oxygen.

1. Oxygen concentration.
2. Moisture content.
3. Carbon monoxide content.
4. Pressure.

A combination instrument which would make the desired determination and which incorporated measuring devices already developed was constructed.

In the operation of oxygen-generating plants, it is sometimes desirable to follow closely the temperature from ambient to the boiling point of oxygen in certain parts of the apparatus. The development of a suitable thermometer which could be manufactured without undue tedium of calibration is described.

The operation of such portable equipment demanded the availability of a liquid level gauge not subject to common shortcomings of manometers. A dial gauge for this use was developed.

[a] Technical Aide, Division 11, NDRC.

14.2 THE PAULING OXYGEN METER

14.2.1 Introduction

When testing oxygen supplies, following the operation of oxygen generating units, testing breathing mixtures, and conducting numerous other tests, the need existed for an instrument which could measure and indicate the partial pressure of oxygen in a mixture of gases. Further advantages were to be obtained from a compact portable instrument that would give rapid and continuous determinations without chemical manipulations. An instrument was proposed for this purpose, the operation of which would depend on the extraordinarily high magnetic susceptibility of oxygen.

Most gases are diamagnetic; that is, they tend to be repelled from a magnetic field. Only a very few gases are paramagnetic and tend to be attracted into a magnetic field, and of these, oxygen is the only common gas. It is a very important circumstance that the magnitude of the magnetic susceptibility of oxygen is many times greater than that of any other common gas. As an example, the volume magnetic susceptibility of oxygen at standard conditions, 142×10^{-9} cgs, may be compared with that of nitrogen, -0.40×10^{-9} cgs, which is representative of the diamagnetic gases. Because of this relatively high susceptibility of oxygen, the susceptibility of a gas mixture is much more strongly influenced by a change in its oxygen content than by an equal change in any other component, and, in fact, if the oxygen content exceeds a few per cent the susceptibility of the mixture is closely proportional to the partial pressure of oxygen.

The forces produced by the action of magnetic fields upon small volumes of gases are proportional to the susceptibilities of the gases and are very small. This is true even in the case of the most strongly magnetic gas, oxygen, at ordinary pressures in the strongest magnetic fields obtainable in the laboratory. The smallness of these forces gives rise to a number of problems which had to be considered in the development of the oxygen meter.

The condition of equilibrium is determined by the following equation:

$$K\theta = H \frac{dH}{d\theta} (K_t - K_m) V r \qquad (1)$$

in which K is the torsion constant of the supporting quartz fiber and θ is the angular displacement of the test body. H is the magnetic field strength, $dH/d\theta$ is the angular field strength gradient, K_t is the volume magnetic susceptibility of the test body, K_m is the volume magnetic susceptibility of the surrounding medium, and V is the volume of the test body, r is the effective radius.

14.2.2 Description and Method of Constructing

EXPERIMENTAL MODELS[4]

A small glass dumbbell 1.4 cm long with spheres 4 mm in diameter is mounted upon a quartz fiber, 8 μ in diameter, as shown in Figure 1. A small mirror is included in the dumbbell assembly.

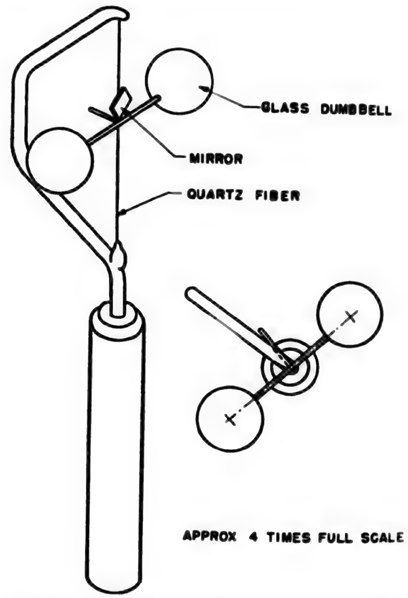


FIGURE 1. Completed suspension for Pauling oxygen meter.

The dumbbell assembly is then mounted in a strong, inhomogeneous magnetic field provided by one or two Alnico permanent magnets, as shown in Figure 2. The test body, or dumbbell, with attached mirror is arranged to rotate through regions of varying magnetic field strength by twisting and untwisting the fiber.

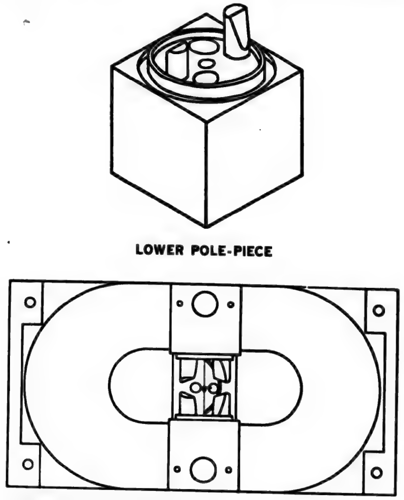


FIGURE 2. Assembly of magnets, pole pieces, and suspension.

METHOD OF CONSTRUCTING THE SUSPENSION[b]

The steps involved in making a suspension will be discussed in the following order: making fibers, making forks, stringing forks with fibers, straightening and stretching fibers, testing mounted fibers, blowing bubbles, sizing bubbles, making dumbbells, testing dumbbells, making mirrors, assembling suspensions, and balancing suspensions.

Making Fibers. The torsion fibers are made from clear fused quartz rods. Whatever the original size, a rod is first drawn out to a diameter of about 1 mm. Slight contamination of the quartz greatly reduces its strength. A single dust particle on a fine quartz fiber will almost always cause the fiber to burn apart in the flame. The torch used for blowing fibers has a $\frac{1}{16}$-in. cylindrical orifice and burns a mixture of oxygen and natural gas.

A fiber is drawn to a length of about 3 ft, which is usually 50 to 150 μ in diameter. The final step is the reduction of the coarse fibers to fine fibers ranging from 3 to 10 μ in diameter. For this operation the oxygen supplied to the torch is reduced until a flame 15 or 20 in. high with a little white at the top is obtained. One of the coarse fibers is heated and drawn vertically in this flame to the desired diameter of 3 to 10 μ. Because of diffraction effects, fibers of sizes useful for suspensions appear colored when viewed as described. In the largest usable sizes the colors are very pale; in the smallest they are quite brilliant.

Making Forks. The forks, or quartz yokes, on which the fibers are strung are made from quartz rod about 1 mm in diameter. The quartz rods are cemented into brass bushings using mixture of bakelite, rosin, shellac, and a little alcohol, and then baked in an oven at 120 C.

The bushing is held horizontally in a pin vise which may be rotated in such a manner that all bends may be made by the action of gravity when the rod is heated at the appropriate point. The form and dimensions of a typical fork are shown in Figure 3.

Stringing Fibers on Forks. The operation of fusing the fine quartz fibers to the quartz forks must be carried out in a place free from dust and air currents. The work is observed under the lowest power of a binocular microscope. A fiber of convenient length is selected and attached to the fork by means of micro manipulators after the fork tips have been softened with a torch flame.

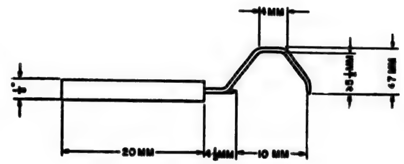


FIGURE 3. Method of making forks.

Straightening and Stretching Strung Fibers. The purpose of these operations is to align the quartz fiber with the axis of the brass bushing and to put it under a slight tension. The strung fork which is to be straightened is held in a small lathe-like jig by clamping the bushing of the fork in a collet. This mounting may be rotated by a hand wheel. Operations are observed with a binocular microscope. Various portions of the fork may then be softened with a torch flame and manipulated until the two ends of the fiber are aligned with the bushing axis within 0.005 cm.

[b] The methods of construction are only outlined here. Recourse should be had to the reference report[4] for a full description of exceptionally neat micro manipulations.

After the strung fork has been straightened it is necessary to put the fiber under a slight permanent tension. With the fork still in the jig, the tail stock is brought near the end of the fork and clamped into place. The screw in this tail stock is then turned until the tip of the fork is bent 0.0025 cm toward the bushing (0.0037 cm for smaller fibers). The knob of the fork is heated until the fiber is drawn taut, the tail stock is withdrawn leaving the fiber under tension, and the mounted fiber is ready for testing.

Testing of Mounted Fibers. The first test that is applied to strung forks is a very simple one. A suitably bent quartz rod weighing about 50 mg must be lifted by the fiber, while horizontal, at its center. The hook which is attached to the weight is coated with fused silver chloride where it touches the fiber in order to minimize the possibility of scratching the fiber.

The determination of the relative torsion characteristic, or *torque* of the fiber is made as follows. A small standard size quartz rod is temporarily fastened by one end to the center of the fiber so that the rod hangs vertically when the fiber is horizontal and untwisted. The angle through which the fork must be rotated in order to cause the attached rod to deviate from the vertical by a standard angle is then read from the dial of the spindle which holds the bushing. The difference between the measured angle and the standard angle is called the *torque* of the fiber; it is inversely proportional to the torsion constant of the fiber.

The quartz rod which is used for this test is specified quite arbitrarily, to be 3 mm long and 0.100 mm in diameter. The standard angle to which the rod is made to deviate from the vertical is 58 degrees.

Blowing Bubbles. It is very desirable that the glass bubbles which are to be used for making the small rotating test body (the dumbbell) be made to conform to certain specifications. They must be held to reasonable tolerances of shape, size, and weight. They should be as light as possible and still sufficiently strong to withstand pressure differences of an atmosphere or more between inside and outside. It is often desired that they possess certain magnetic properties.

These bubbles are about three mm in diameter. With the short stem that is left on them to form half of the dumbbell cross bar, they weigh about 0.7 mg each.

It has been found that these small bubbles can be blown more easily from laboratory soft glass than from pyrex glass. A piece of soft glass tubing is first drawn out into a thin-walled capillary 0.5 mm in diameter. A natural gas flame about ½ in. high and containing little or no primary air (air introduced at the base of the burner) is used. The tip of the capillary tube is inserted into the flame and melted to form an extremely small ball of glass on the end of it. The tube is jerked axially from the flame and almost simultaneously is blown with a quick puff of air from the mouth to form a bubble. The timing of this manipulation must be accurate and is attained only with practice. The blowing is done with the lips and the tongue in order to obtain the quickest and most powerful puff of air. The oversize, aspherical bubble is then shrunk to the correct size and to a spherical shape by rotating it well above the small Bunsen flame.

The above procedure is probably the most difficult of the procedures involved in making a Pauling oxygen meter. However, with practice a good manipulator can learn to blow acceptable bubbles at an average rate of one or two dozen per hour. Since only two are required for each meter, exclusive of breakage, the time required to produce bubbles is not disproportionately large.

A new improvement in the manufacture of bubbles which considerably lessens the required degree of skill has been developed by the A. O. Beckman Laboratory. A spring-operated valve device simultaneously blows out the gas flame and introduces into the capillary tube the correct quantity of air. The bubbles so obtained are shrunk to the desired size and shape by the procedure described above.

For special purposes it is sometimes desired to obtain dumbbells with a higher paramagnetic susceptibility than can be obtained from soda glass bubbles filled with oxygen. One way of obtaining such dumbbells is to make them of bubbles made of paramagnetic glasses. Glasses containing iron, for example, may exhibit a positive net susceptibility; special glasses containing iron might be made up. For experimental work it was found to be more convenient to test the magnetic properties of a number of samples of glass and to keep these tested samples on hand than to make up special glasses. Old green-glass champagne bottles were found to give a great variety of magnetic susceptibilities.

Sizing Bubbles. When a batch of bubbles has been prepared the bubbles must be sorted according to size. This sorting involves a volume determination which is carried out by weighing the bubbles first in air and then immersed in alcohol. For this purpose a very sinple type of quartz fiber balance is used.

Making Dumbbells. The three parts of a dumbbell are the two bubbles, matched in size, and a balancing rod. The magnetic properties desired for the dumbbell determine the kind of glass which must be used for the bubbles and the composition of the gas which must be sealed into the bubbles. A commonly used dumbbell is made of ordinary soft glass bubbles filled with air. If some other gas is to be used to fill the dumbbells, the bubbles are placed in a vacuum desiccator. The desiccator is evacuated and the filling gas is admitted up to atmospheric pressure. The ends of the bubble stems are then sealed with a small torch as quickly as possible after opening the desiccator. The bubble stems are cut off with the 0.008-in. torch to give an overall length of 4.5 mm for the bubble and stem. The balancing rod material is a coarse glass fiber, about 0.1 mm in diameter, usually drawn from a magnetically neutral soft glass. The two bubbles and the balancing rod are held in separate holders; at least two of these holders are attached to micro manipulators.

Alignment of the bubbles and balancing rod prior to sealing them together should be done with the greatest possible accuracy. The object of careful alignment is to make the dumbbell such that when it is assembled in a suspension the fiber will pass very near to the center of volume of the combination of the dumbbell and the mirror (which may be referred to collectively as the dumbbell). Gravitational balance can be perfected after the suspension is assembled.

Meters having suspensions in which the center of volume does not fall quite close to the fiber will exhibit an undesirable buoyancy effect when used in gases having densities different from atmospheric air. The actual fusing or sealing is done by bringing the 0.008-in. torch, its flame held vertical, from the operator toward the junction. The dumbbell is dropped immediately into a bottle of alcohol.

Testing Dumbbells. Before dumbbells are removed from the bottle of alcohol into which they have been dropped, they are tested for strength and for leaks. Suction is applied to the mouth of the bottle until the pressure is reduced to about the vapor pressure of alcohol, taking care that the alcohol is not permitted to boil violently. It is also desirable to test the dumbbells against external pressure. In a normal test compressed air at 10 or 15 psi would be applied; however, for special meters it might be desirable to select dumbbells that would withstand greater pressures. Under these treatments weak bubbles burst or collapse and leaky bubbles fill with alcohol and submerge. The dumbbells which have been unaffected by these tests are rinsed with fresh alcohol and are ready for further operations.

Before using the dumbbells in making completed suspensions it is often desirable, although not always necessary, to determine their magnetic properties, as these may influence the choice of values of the other parameters of the suspension. This is done by assembling and roughly balancing a temporary suspension using a dumbbell to be tested and a fiber which is repeatedly used for this purpose. This suspension is placed between a pair of pole-pieces which are attached to an electromagnet. In general, the passage of current through the electromagnet will cause a deflection of the dumbbell. The partial pressure of oxygen which reduces the deflection of the dumbbell to zero is equivalent to the average volume magnetic susceptibility of the dumbbell, expressed in units of oxygen partial pressure, at the position of the field occupied by the dumbbell, and at the temperature at which the experiment is conducted.

Making Mirrors. The small mirrors used in the suspensions are about $\frac{1}{16}$ in. square and about 0.003 in. thick. They should be made as thin as possible without being too fragile. Glass, fused quartz, and crystal quartz have all been used. Fused quartz is particularly desirable because its low coefficient of thermal expansion prevents it from cracking under the influence of the high temperature gradients which are present during the process of sealing the dumbbell, fiber, and mirror together.

The small squares of glass or quartz are thoroughly cleaned and dried. They are then given a metallic coating by evaporation of metal onto them in a high-vacuum chamber. Aluminum is not very satisfactory because it reacts with the silver chloride which is used in cementing the suspension together. Palladium is satisfactory in this respect; it also has the advantage of being paramagnetic while quartz and glass are diamagnetic so that mirrors can be made that are approximately magnetically neutral.

Assembling Suspension. The brass bushing on the fork is held in a collet in the spindle of a jig. The dumbbell is fastened with paraffin to a holder which can be moved horizontally by two screws, one producing movement parallel to the axis of the spindle and the other producing movement perpendicular to

it. The mirror is held on a flat silver plate (to give good heat conduction) at the end of a brass rod. The work is observed under a microscope.

After the parts have been fastened to their holders they must be brought together into the correct positions for sealing together. Sealing is done with fused silver chloride.

The angles between the fork and the dumbbell, between the mirror and the dumbbell, and between the mirror and the fiber depend upon the optical system and mechanical arrangements of the model of the oxygen meter for which the suspension is being made, and upon the particular range which is desired. The required fiber torsion constant and the required dumbbell susceptibility depend upon the characteristics of the magnetic field in the particular model and upon the particular range which is desired. The dumbbell must often be further selected on the basis of its temperature coefficient of volume magnetic susceptibility if it is to be used in a temperature-compensated instrument.

Balancing Suspensions. For testing balance, a suspension is shielded completely from air currents by a transparent celluloid cover which fits over the spindle of the assembly jig and rotates with it. On the flat closed end of this cylinder are engraved a set of parallel lines which are useful in observing relative motions of the dumbbell and the fork. The ultimate criterion for perfect balance is the lack of any change in the relative positions of the dumbbell and the lines on the cap when the spindle is rotated through 360 degrees.

Coarse balancing is accomplished by adding very minute droplets of a low melting lead borate glass to the appropriate place on the dumbell. Powdered lead borate is picked up, melted, and applied with the 0.002 in. platinum hot wire.

Fine balancing is accomplished by evaporating traces of silver chloride or iodide or a mixture of the two from a platinum hot wire (0.01 in. in diameter) onto the dumbbell.

The dumbbell must be balanced in all planes which include the quartz fiber. It will be so balanced, however, if it is balanced in any two of them.

The Completed Suspension. A completed suspension is shown in Figure 4.

The Magnet and Pole Pieces

The permanent magnets are made of Alnico V. It is customary to use a pair of symmetrically placed magnets weighing about 5 oz each giving maximum effective field strength of about 5,000 oersteds. However, a sensitive meter has been designed and built using a single magnet weighing about 6 lb (Model K).

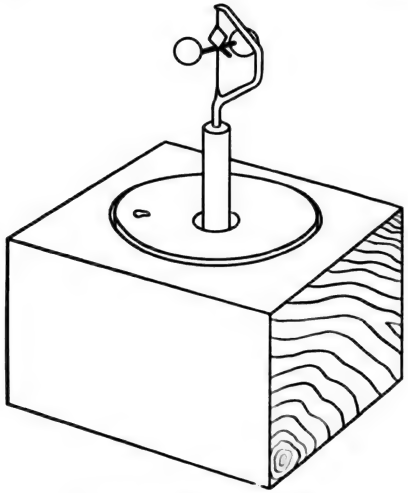


Figure 4. Completed suspension.

Various shapes of pole pieces have been tried. A suitable shape must not only be satisfactory magnetically but must also meet certain requirements imposed by the attached mechanical and optical systems. Three types of pole pieces have been found satisfactory and useful in different applications. These three types are illustrated in Figures 2, 5, and 6. The first two types have been used with the smaller magnets and seem to be roughly equivalent from the standpoint of field characteristics; mechanical considerations have dictated the choice between these two types for different applications. Figure 6 shows the type of pole piece used with the large magnet mentioned above (Model K).

A magnetizer was built according to a design developed in the Bell Telephone Laboratories.[27] This was used to magnetize the large magnets which are used in the Model K meters. Figure 7 is a schematic circuit diagram of the magnetizer. A battery of electrolytic condensers, of total capacity 2,600 μfd, is charged to about 350 volts by means of a transformer and rectifier and is discharged through the magnetizing coil (six turns of No. 8 copper wire) around the magnet by means of an Ignition tube (General Electric GL-415).

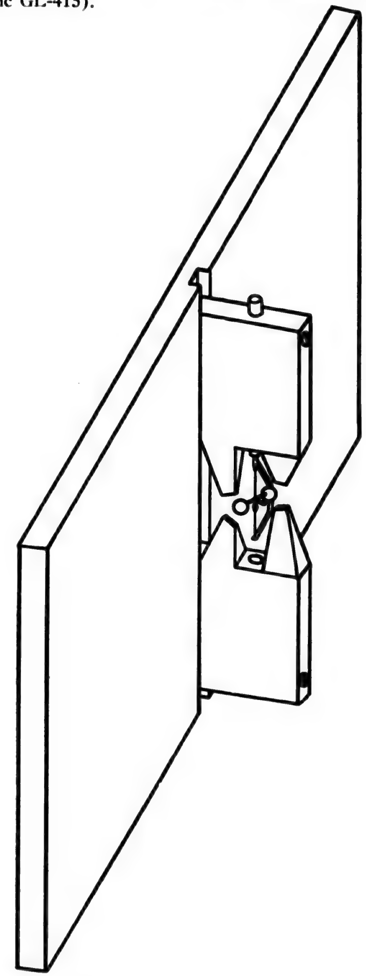


Figure 5. Pole pieces and backplate—Model P. Magnets removed.

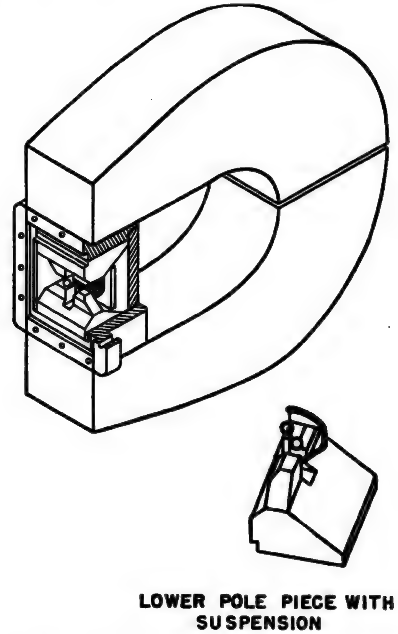


Figure 6. Model K: Magnet and test chamber, with pole pieces and suspension. Window, cover and rubber gasket removed.

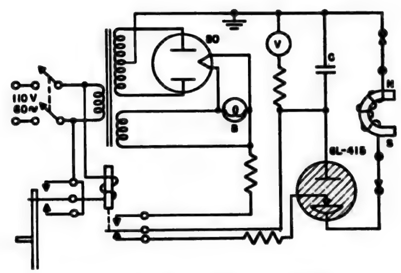


Figure 7. Circuit diagram of magnetizer.

THE OPTICAL SYSTEM, FLOW CONTROL, AND TEMPERATURE CORRECTION

The test body and magnet are mounted in a cabinet together with suitable devices for controlling the flow of sample gas and for observing the deflection of the test body.

The flow to the sample chamber may be controlled by a needle valve and flow meter of the "Rotameter" type (as in Model P) or by a sensitive pressure regulator (plenum chamber) and orifice (as in the combined Bureau of Standards moisture indicator and oxygen analyzer). In later models[7] the gas sample flows through a passage-way which connects with the sample chamber through a porous diffusion disk. This last method has the advantage that the reading is independent of flow over a considerable range of flows and the test body suspension is not subject to injury by high flow rates. It has the disadvantage that an appreciable time (45 to 60 sec) is required to established equilibrium through the diffusion disk.

The test body suspension and magnet poles are enclosed in a gas-tight chamber with entrance and exit ports for the gas sample. A lens window in this chamber forms part of the optical system in which the image of a lamp filament is focused upon the mirror on the suspension and thence to a scale graduated in millimeters of partial pressure or per cent of atmosphere, as desired.

The fact that the magnetic susceptibilities of both oxygen gas and the dumbbell depend on the temperature implies a temperature effect on the reading of the meter. Three methods of making the oxygen meter usable at different ambient temperatures have been used. The most direct method is to make calibrations at various temperatures and to provide correction tables or graphs. Another method involves compensating the meter for temperature effects. To do this, the magnetic field strength is caused to vary with temperature in such a manner as to counteract the temperature dependence of the susceptibility of oxygen. It is also necessary to use a dumbbell which has the same temperature behavior as has the surrounding gas. The desired variation in field strength is obtained by placing across the permanent magnet a shunt made from one of those iron-nickel alloys which have very high temperature coefficients of permeability at ordinary temperatures. The third method of eliminating the temperature effects is to maintain the meter at a constant temperature by means of a thermostat.

14.2.3 Deflection-Type Instruments Developed at California Institute of Technology

Early Models. The first complete oxygen meter, other than the purely experimental laboratory apparatus, was the one known as Model A.[c] This was calibrated to cover a range of 0 to 160 mm of oxygen.

The next six meters constructed were designated as Model B. Model C, which included two meters very similar in appearance to Model B, differed from B chiefly in having two magnets instead of one. Both Model B and Model C were equipped with a by-pass valve so that the flow of sample could be cut off while a reading was being taken.

The Model P Pauling Oxygen Meter. The next model developed after Model C was Model P, a fairly rugged laboratory instrument. About thirty of them were constructed at the California Institute of Technology and sold for various war purposes.[d]

One of these meters is shown in Figure 8. The walnut veneer cabinet has dimensions of about 7x7x12 in. The total weight of the meter is about 12 lb. On the black bakelite front panel of the instrument may be seen the calibrated oxygen partial pressure scale, the thermometer scale, the power switch, the needle valve control handle, the Rotameter flow indicator, and the nipples by means of which the gas to be analyzed is caused to flow through the meter.

The A. O. Beckman Laboratories took over the manufacture of Model P meters in the summer of 1942. This model is not being currently produced; it has been superseded by models which have been more recently developed by this concern.

Model D, the "Submarine Model." A promising application of the oxygen meter is its use in measuring the oxygen content of the ambient air in a submarine to determine its respirability. For this purpose a meter, designated as Model D, was designed and constructed. It differs from Model P primarily in that the gas sample enters the analysis chamber by diffusion and convection, direct from the surrounding atmosphere. The test chamber is electrically heated in order to keep it above the ambient temperature of the submarine and thereby

[c] Dr. A. O. Beckman and his associates are currently producing a Pauling oxygen meter which they designate "Model A" and which should not be confused with the o[ne] here described.

[d] Most of the developmental cost and all of the constructi[on] costs of these Model P meters were provided by funds oth[er] than those available under NDRC contracts.

FIGURE 8. Model P Pauling oxygen meter.

prevent condensation of water in the meter when it is used in atmosphere of high relative humidity. This heating also promotes convection and improves the gas circulation, thereby reducing the time required for the meter to register a change in the oxygen content of the ambient atmosphere. The optical system is similar to that of Model P but utilizes an illuminated slit as a light source.

Model L, the "Airplane Model." A possible application of the oxygen meter is its use in airplanes to test oxygen equipment used in high-altitude flying. A meter which is to be used for this purpose should be compact, light in weight, ruggedly constructed, well protected against vibration, and operable over a wide temperature range. An experiment was carried out in which two Model P oxygen meters were carried to an altitude of 30,000 ft in a Liberator bomber and tested in flight. Both meters performed quite satisfactorily. However, the size, weight, and construction of the Model P meter, which is essentially a laboratory instrument, are not especially favorable for continued use in a flying airplane.

A meter, designated as Model L, has been developed specifically for such use. The cabinet and most of the parts are of aluminum, for considerations of weight; the entire instrument weighs less than 5 lb. The meter is very compact; the overall dimensions are $3\frac{1}{4}$x$6\frac{1}{2}$x8 in.

The test chamber and magnet assembly, the shield frame, the scale support, and the optical system form a rigid unit which is mounted, by means of Lord double-rubber mountings which protect it against vibration and shock.

The Model K Oxygen Meter. With the aid of the Bell Telephone Laboratories a magnetic circuit has been designed which employs a magnet of Alnico V weighing about 6 lb, and a suitably designed test chamber (Figure 6). The magnet was remagnetized, with the test chamber in place. A maximum field strength of about 11,000 oersteds was measured between the pole pieces. Since the magnetic forces acting upon the dumbbell vary with the square of the maximum field strength for a given field shape, these magnetic forces should be four or five times as great as in other models, permitting increase by a factor of the order of four or five in the torsion constant of the

fiber. One model of the oxygen meter Model K employing such a magnet and test chamber has been developed.

Because of the inconvenience of winding a magnetizing coil on the magnet with the test chamber in place, and because of the necessity for remagnetization after every occasion of removing the test chamber or a pole piece, it would be desirable to provide a means of installing and adjusting the suspension in the test chamber without first removing the test chamber or either pole piece from the magnetic circuit.

14.2.4 Deflection-Type Instruments Developed by the A. O. Beckman Company[7]

Model P. The Model P instrument is described in detail in the preceding section.

Many of the instruments had temperature compensators, consisting of a magnetic shunt made from an alloy with a high negative temperature coefficient of magnetic permeability at ordinary temperatures. Approximately 30 instruments of this type were made at the California Institute of Technology and 94 instruments were made by the Arnold O. Beckman Company. As the attempt to achieve temperature compensation by the magnetic shunt was not very successful, in many of the later instruments the temperature compensator was replaced by a thermoswitch and an electric heater which maintained the analysis cell at constant temperature.

The Model P instrument was made in various ranges, including the following: 0 – 35 mm, 0 – 160 mm, 0 – 200 mm, 0 – 250 mm, 0 – 400 mm, 0 – 500 mm, 0 – 600 mm, 0 – 800 mm, 650 – 760 mm, and 580 – 800 mm.

Model S. This model, like the Model D, was designed specifically for use in submarines or other enclosed spaces where it is desired to analyze the ambient air. The internal construction of the instrument is essentially similar to that of the thermostated Model P instrument. The needle valve and flow meter are omitted. Sampling of the ambient air is obtained by diffusion and thermosyphon action. The temperature of the analysis cell is held constant at approximately 140 F. The inlet and exit connections to the analysis cell are protected by a glass-wool dust filter and magnetic filters to remove any magnetic particles which might be present.

The completed instrument is housed in a steel case $6\frac{1}{2}$x7x$4\frac{1}{2}$ in. The internal assembly is protected from shock damage by mounting on rubber shock mountings. The instrument successfully passed the standard Navy vibration and shock tests.[28]

Model A. The Model A instrument is a portable laboratory instrument for general use where readings in oxygen partial pressure units are desired. A constant temperature analysis cell having cylindrical glass walls is used. No needle valve or flow meter is included, as the instrument is designed to accommodate widely varying flow rates through the use of restricting orifices and a built-in by-pass device which automatically by-passes part of this sample stream whenever this rate of flow is excessive. The instrument is housed in a walnut carrying case $7\frac{1}{4}$x$7\frac{1}{4}$x$8\frac{3}{4}$ in.

Model T. A small meter, Model T, weighing but $2\frac{1}{2}$ lb, and measuring 5x$2\frac{1}{2}$x6 in., was developed for testing the atmosphere of oxygen tents and other therapeutic apparatus. Gas samples are drawn into the test chamber through small diameter rubber tubing by means of a rubber bulb. An additional mirror has been inserted in the light path to increase its length. By reason of the lengthened optical path, the total angular rotation in Model T is only 8 degrees, compared to 30 degrees in Model A. It has been found possible under these conditions to reproduce component parts so nearly uniform that individually calibrated scales are not required.

14.2.5 Null-Type, Electrostatically Balanced Instruments Developed at Arnold O. Beckman Company

Electrostatic Balance

The deflection-type instruments are particularly suited for applications where oxygen partial pressure readings are required. In many cases readings in oxygen percentage are desired. Oxygen percentages can be obtained, of course, by dividing the oxygen partial pressure by the total pressure of the gas in the analysis cell, but this procedure is often very inconvenient. For industrial applications, where continuous recording and automatic control are desired, means for obtaining oxygen content directly in percentages would be very valuable. Instruments incorporating such means were developed and are known as electrostatic models or null-type instruments.

In these instruments a new force is added to the

magnetic and torsional forces involved in the deflection-type instruments. By establishing an electrostatic potential between the rotable test body and suitably placed electrodes, electrostatic forces of the same order of magnitude as the magnetic and mechanical forces involved are added. This additional, easily adjustable parameter makes it possible to standardize the oxygen meter at the ambient pressure with some known reference gas, so that subsequent readings on unknown gases will be indicated directly in terms of oxygen percentage. The use of an electrical potential, furthermore, makes possible the use of conventional chart recorders and process control equipment. These instruments have proved to be very useful, particularly in refineries for the production of aviation gasoline and toluene.

Electrostatic Null Method No. 1, Square Law. In the deflection-type instruments there are two forces affecting the rotation of the dumbbell-shaped test body, namely, the magnetic force and the torsional mechanical force of the quartz fiber. If an electrostatic field is introduced in addition to the magnetic field, charges will be induced on the test body and the test body will thereby be subjected to an electrostatic force. The electrostatic field can be produced conveniently by applying a potential between the magnetic pole tips. With the dimensions and geometry of the conventional instrument, potentials of the order 20 to 100 volts produce electrostatic forces of the same order of magnitude as the magnetic forces involved.

Electrostatic Null Method No. 2, Linear Relation. The electrical circuit of this type may be compared to the conventional Wheatstone bridge, in which two arms of the bridge are photocells. Since, with a given voltage, the current flowing through a photocell changes in relation to the amount of light falling upon it, the photocell may be considered to be a variable resistor. With a galvanometer of sufficient sensitivity to work with high impedance photocells, a simple Wheatstone circuit could be used. By the use of two electronic tubes in a cathode-follower arrangement, circuit impedances can be matched so that a conventional low resistance voltmeter can be used as the indicating instrument.

The operation of the circuit is as follows. With identical phototubes equally illuminated, the 90-volt D-C potential will be divided equally across the two photocells. The grids of the two electronic tubes, therefore, will give the same potential, namely 45 volts. The cathode of the tubes will also be of the same potentials, slightly above 45 volts, so that the voltmeter will read zero. Assume that the mirror rotates so that the lower phototube receives more illumination. The potential of the first grid will be decreased, whereas the potential of the second grid remains at 45 volts. Consequently, the voltmeter will indicate the difference of potentials between the two cathodes just as the galvanometer would indicate a difference in potential in the simple Wheatstone bridge circuit.

The test body is gold-plated for electrical conductivity and is electrically connected through the quartz fiber to the first cathode. As the first cathode potential decreases, the potential of the test body likewise becomes less, thereby producing an electrostatic force which tends to restore the dumbbell to its original position. The test body does not return exactly to its original position but, as in the case of the square law method, an angular position minutely different from the null position suffices to generate a D-C potential of the proper magnitude to balance the magnetic and torsional forces acting on the test body.

The condition of static balance in the electrostatic instruments is defined by the equation

$$k\theta = L_m + L_e$$
$$= A\left(V_3 - \frac{V_1 V_2}{2}\right) + B(V_2 - V_1)^2, \qquad (2)$$

where L_m is the magnetic torque given by the right-hand member of equation (1), L_e is the electrostatic torque, A and B are the angular rate of change of capacity between the test body and electrodes and between the electrodes, respectively, and V_1, V_2, and V_3 are the potentials on the electrodes and test body, respectively.

By means of the photocells and the appropriate circuit connections, the variational suspension voltage is made proportional to the angular rotation of the test body and the stabilizing effect of *negative feedback* is obtained. The output voltage V, measured between the test body and a fixed point in the circuit is given by

$$V_0 = \frac{L_m L^\circ_e}{A(V_2 - V_1)}, \qquad (3)$$

where L°_e is a constant electrostatic torque dependent upon the zero setting of the instrument.

Model R. This was the first of the electrostatic instruments. In these instruments the voltage between the test body and the electrodes required to maintain the test body in its null position varies as the

square with respect to the change in oxygen partial pressure. Because of this square law relation, the Model R instruments have always been used with the electrodynamometer type of recording voltmeter in which the deflection is proportional to the square of the applied voltage. The combination results in an approximately linear percentage scale.

Model E. In this instrument the electrical circuit is such that an accurately linear relation exists between the null-balance voltage and the change in oxygen partial pressure. There are obvious advantages in a linear scale for calibration and standardization, as well as in use. The Model E is designed for laboratory use and is a multi-range instrument, having five ranges of 0 to 5%, 0 to 25%, 25 to 50%, 50 to 75%, and 75 to 100% oxygen. Standardization for the ambient barometric pressure is easily made with the aid of dry air or other reference gas. The instrument is adjusted to a null balance by manual operation of a potentiometer dial, which is calibrated directly in oxygen percentage.

Model F. In this instrument also a linear relation exists between voltage and change in oxygen partial pressure. The instrument differs from the Model E, however, in that manual adjustment of the balancing voltage is not required. The test body is automatically maintained in null position by a self-balancing electronic circuit. The balancing potential is shown continuously on an indicating voltmeter.

Model G. This model is substantially identical with the Model F except that the indicating meter is replaced by a potentiometer-recorder. These instruments have been of particular interest in the low range, 0 to 5%, for catalyst regeneration control in oil refineries, and in the high range, 95 to 100%, in plants for the production of oxygen.

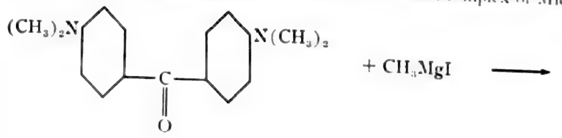
Aircraft Model. This experimental flight model is an adaptation of the linear electrostatic Model F designed for operation from portable dry-cell batteries. The analysis unit, which is 5¾ in. wide, 5¾ in. long, 5⅞ in. high and which weigh 4 lb, 10 oz, is attached by rubber shock mountings to a battery case. The complete instrument, including the batteries, weighs 18 lb, 8 oz. The useful life of the batteries is about 100-hr continuous operation.

Oxygen partial pressure is indicated continuously on a microammeter built into the analyzer. Calibration adjustments are as on Models E, F, G, with the addition of a means of suppressing the zero point any amount up to about 0.75 atm air.

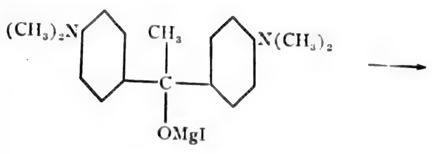
14.3 INSTRUMENTS FOR DETERMINING MOISTURE CONTENT OF GASES

14.3.1 Chemical Method[15]

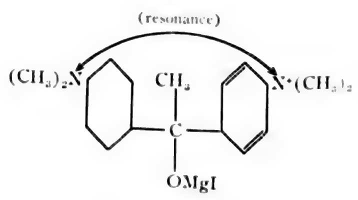
A survey of chemical tests for the detection of water vapor was made, but none was satisfactory for the high sensitivity needed (the detection of 0.01 to 0.010 mg per l). An investigation was therefore made of a series of compounds of ketones and Grignard reagents which can form internal ions accompanied by the development of intense color. This internal rearrangement is induced by the high dielectric properties of water. The most useful compound is a complex of Michler's ketone and Grignard agent.



Michler's Ketone

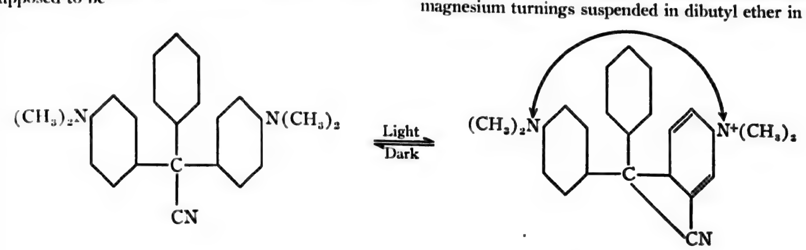


Colorless MeMMgI



Colored MeMMgI

The constitution of colorless MeMMgI has by no means been established, and that for the colored compound is purely hypothetical, based on the coloration of malachite green leucocyanide by light, which is supposed to be



Malachite green leucocyanide (colorless)

Malachite green cyanide (colored)

A related reagent which may be designated EtMMgBr was made from ethyl bromide instead of methyl iodide. This compound is so much more sensitive than MeMMgI that it could be used for detecting dew points in the neighborhood of —75 C. This material was far more sensitive than required at ordinary temperatures and therefore no work was done with it. It should be noted, however, that it will give satisfactory tests with commercial oxygen at ambient temperatures at —45 C and so could be used under arctic conditions. A compound EtMMgCl may be even more sensitive, but this was not investigated.

A reagent made from benzophenone and iodobenzene is less sensitive to water and is, therefore, suitable for testing gases with higher moisture content. The compounds which were investigated are listed in Table 1 together with a sensitivity, expressed in relative exposure time for coloration compared to MeMMgI.

TABLE 1. Reaction products of Grignard reagents and ketones which are sensitive to moisture.

Grignard reagent	Ketone	Relative times	Color change
1. Ethyl magnesium bromide (EtMMgBr)	Michler's	0.1	Colorless to green
2. Methyl magnesium iodide (MeMMgI)	Michler's	1.0	Colorless to light blue
3. Methyl magnesium iodide	Benzophenone	25	None at 25 minutes
4. Phenyl magnesium iodide	Michler's	5.0	Yellow to dark blue-green
5. Phenyl magnesium iodide	Benzophenone	4.0	Colorless to rust

Preparation of Reagent. The Grignard reagent was prepared from anhydrous methylal iodide and magnesium turnings suspended in dibutyl ether in an atmosphere of dry nitrogen. The Grignard reagent was added to an anhydrous solution of Michler's ketone (tetramethyl-diaminobenzophenone) in benzene.

Apparatus. A glass ampule was prepared from ¼-in. tubing about 4 in. long. One end of the tube was drawn to a tip and sealed off. Retaining plugs of woven glass fiber were inserted with dry sand. After baking out, a measured portion of the reagent was introduced into the open end of the tube in an atmosphere of dry nitrogen, and this end of the tube was immediately drawn to a tip and sealed. Bench apparatus for introducing the reagent and the sealing of the ampule was designed which doubtless could be extended to large-scale production.

The reagent remains sensitive after heating (in absolutely dry ampules) to 110 C and cooling to —78 C, and after storing for six weeks at 65 C. However, long periods of storage (6 months or more) introduced changes in the calibration of the ampules and indicated discouraging supply problems in the field. This may be in part due to the extreme sensitivity of reagent to moisture and the slow evolution of moisture from the sand support, glass of the container, etc. Silica gel was found to be entirely unsuitable as a support in place of sand, because of the difficulty of moisture removal by ordinary baking procedures.

The apparatus and the method of making moisture determinations is at once very compact and very simple.

Suitable apparatus is shown in Figure 9. This consists of: (1) a coupling for attaching to the cylinder, (2) needle valve which will stand 3,000 psi with a fine adjustment to provide very low rates of flow from this pressure, (3) a holder for the glass ampule with provision for breaking the tips of the ampule after insertion and flushing with gas sample, (4) indicator for flow rate.

FIGURE 9. General view of complete chemical test instrument for moisture detection.

All parts must be made of substances which do not adsorb water; metal is the only safe material. Even with metal, crevices and corners must be avoided because of the difficulty of purging moisture therefrom.

Operation. The operation of the apparatus shown in Figure 9 is as follows. The apparatus is attached directly to a high-pressure cylinder of oxygen, the cylinder valve opened and the needle valve adjusted to give the approximate flow with a blank tube (which may be an ampule from a previous determination) inserted in the ampule holders. A desirable flow is approximately 1 l per min and is indicated by flow meters of the Rotameter type. The blank tube is then removed from the holder and a fresh ampule inserted. After allowing a short interval of time for flushing, the crusher mechanism at each end of the holder is actuated to break the tips of the ampule, the needle valve quickly adjusted for accurate flow and the time observed. Color formation was to occur at the top of the tube and slowly extend downward during progress of the test. The time is recorded for the movement of the color front along a given distance and this is compared with data furnished for the conditions of temperature and flow for the batch of ampules. The boundary condition 0.02 mg per l moisture content was observed to give a movement of the color front of approximately 1 in. in 2½ minutes at normal room temperature.

Several difficulties were experienced with the operation of this instrument.

1. The color boundary was not always sharp or uniform across the diameter of the tube. This was presumably due to channeling of the gas in the sand.
2. A long purging was required when the apparatus was first attached to a cylinder of oxygen.
3. A variation of as much as threefold was obtained by different ampules in determinations upon a single cylinder of oxygen.

Data shown in Table 2 are typical of the results obtained with this apparatus which represents a large number of ampules observed in the apparatus when connected to a single cylinder of oxygen which gave a reading of 0.018 mg per l at the start of the test and 0.024 mg per l at the end of the test by the electrical conductivity methods of the Bureau of Standards (this variation is due to a reduction of the pressure in the cylinder from 1,400 psi to 600 psi during the investigation of the colorimetric moisture tester).

In a further attempt to simplify the apparatus and overcome some of these difficulties, the ampule was reduced in size and increased in uniformity. The apparatus was modified by elimination of the needle valve and substitution of a pop-off connection and by-pass valve before the ampule connection for fine adjustment of the flow in the main cylinder valve. No material improvement in the functioning of the system resulted and it became increasingly evident that storage deterioration in the ampules was a serious problem.

Although the apparatus is extremely compact and the method of analysis is inherently simple, the degree of judgment required in making the reading is extraordinarily great and believed to be unsuited for use by unskilled personnel in the field. Although the apparatus is far less expensive than the Bureau of Standards apparatus in initial cost, the cost of ampule

TABLE 2. Test data on MeMMgI made upon a single cylinder.

Moisture content indicated at 0 to 2½ mark	Moisture content indicated at 2½ to 5 mark
A. Flow rate 1 l per min†*	
0.36 mg per l	0.031 mg per l
0.024	0.023
0.021	0.013
0.024	0.033
0.026	0.024
0.036	0.031
0.024	0.023
0.021	0.013
0.024	0.033
0.026	0.024
0.023	0.023
0.051	0.038
0.031	0.033
0.021	0.023
0.019	0.022
B.‡ Flow rate 0.400 l per min	
0.023	0.023
0.051	0.038
0.031	0.033
0.021	0.023
0.019	0.022
0.030	0.036
0.028	0.039
0.027	0.016
0.037	0.021
0.019	0.017
0.020	0.016
0.018	0.016
0.017	...
0.020	...
0.027	0.022
0.025	0.020
0.022	0.027
0.120 mg/l§	0.04 mg/l
0.027§	0.23
0.32§	0.25
0.34	0.34

* The initial pressure of this cylinder is 1,400 psi and gave a reading of 0.018 mg per l. At the end of observations the pressure was 600 psi and the electrical conductivity method gave a reading of 0.024 mg per l.

† December 29, 1943.

‡ December 31, 1943.

§ The flow was at normal temperature, 78 F. Values were obtained consecutively after connecting the instrument. The instrument was then disconnected, exposed to room air for a few minutes, reconnected and the fourth point measured. The initial pressure was 600 psi (same cylinder as reported in Table 1) and the final pressure 550 psi. Reading on the NBS instrument was 0.024 mg per l before and after tests B.

supplies would be far in excess of the operating cost of the Bureau of Standards instrument.

Suggested Further Development. The chemicals herein described are undoubtedly interesting as indicators for extremely low concentration of moisture. It is believed that in order to make the system useful as a means of determining moisture much work remains to be done upon the physical properties of the system. For example, the flow of the gas through the packed bed of sand needs to be more accurately controlled, inasmuch as this is a time-absorption phenomenon and not an equilibrium condition. Also, it will be necessary to control more accurately the surface of the supporting medium (sand) and the amount of reagent adsorbed thereon. Possibly, if these problems are satisfactorily solved in a low-cost ampule the method will find extensive use in testing a number of dry gases.

14.3.2 Frost Point Instrument for Determining Moisture Content of Gases

A moisture-measuring instrument of the frost-point (or dew-point) type gave promise of being very compact and simple to operate in the field, within the range of accuracy required for determining the moisture in cylinder oxygen gas. The method is an improvement over the colorimetric method just described in that it is absolute, no calibration being necessary and no charts being needed in performing analyses. The moisture content is read directly from a gauge dial and the result is independent of variations in ambient temperature, oxygen pressure, and other external variables.

If determinations are made on an accept or reject basis of defined boundary value, for example, 0.02 mg per l, the manipulation of the test apparatus becomes very simple and the time required per determination is of the order of 1 min.

Compressed carbon dioxide is used as refrigerating means (about 5 g per determination, or 1 lb per 100 determinations). This together with small dry cells for the operation of the flashlight bulb constitute all of the supplies necessary for the operation of the apparatus. Four or five l of oxygen gas sample is adequate for a determination.

Experimental apparatus was developed and built[3] by Arthur D. Little, Inc., from which two production models were made; one by the Mine Safety Appliances Company, and one by the Foxboro Instrument Company. Several instruments of each model were produced for examination and testing by the Services.

Design Features and Description of Experimental Model. A frost point instrument for the proposed

use includes three fundamental elements: (1) means for cooling the target on which the dew or frost is to collect and for holding the temperature constant at any desired value, (2) means for measuring the temperature of the target, and (3) an optical system for readily observing small deposits of dew or frost.

The experimental assembly of these elements is shown in Figure 10. The target, a small cylindrical

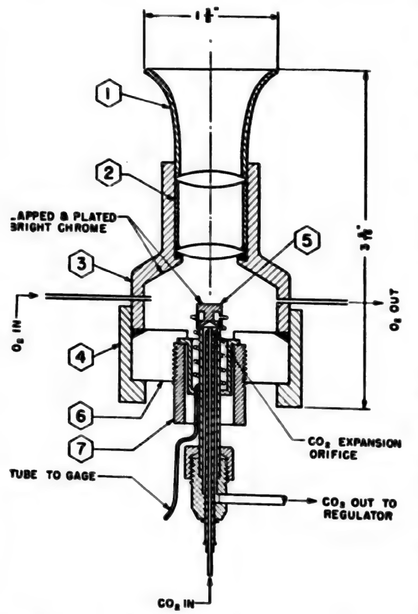


FIGURE 10. Tester body of McMahon dew-point apparatus.

copper plug, is shown at 5. This is enclosed in a chamber through which the gas sample is caused to pass. The target is cooled by impinging upon its lower surface a stream of carbon dioxide from a restricted orifice. The expansion takes place from full cylinder pressure for carbon dioxide to a lower pressure and hence, fixed temperature, controlled by a regulator to regulate the temperature of the target. The target is provided with a ring-shaped cavity connected by fine capillary tubing to a pressure gauge and charged with carbon dioxide to constitute a vapor pressure thermometer for measuring the temperature of the target. The target is directly illuminated from light passing through a transparent window 6 and deposits are observed through telescopic systems 1 and 2. Not shown in Figure 10 are connection facilities for carbon dioxide and gas sample, light source for illuminating target and pressure regulator, and for adjusting expansion pressure of carbon dioxide at the target. Figure 11 shows the relative position of the component parts of the instrument within the case.

Control of temperature is accomplished by allowing compressed carbon dioxide (from the gas phase above liquid) to expand through a small orifice. The stream of cold carbon dioxide, partially liquefied, is directed against the underside of a small copper block, the target 5. Because of the excellent heat transfer coefficient between the copper block and the stream liquid of carbon dioxide spray (approximately 5 g per min flow), the target is cooled to within a few degrees of the temperature of the spray within 20 to 30 sec. By controlling the pressure of the expanded carbon dioxide, a temperature is fixed at any desired value as shown in Figure 12. Operation is best when the pressure after expansion is greater than 5 atm abs, the triple point for carbon dioxide, since solid carbon dioxide will not be present to clog the apparatus. The triple point appears to lie quite close to the boundary frost point for which the moisture content is 0.020 mg of water per l STP. Figure 12 is the vapor-pressure curve for carbon dioxide.

Figure 13 is the frost-point curve for ice in which the vapor pressure is expressed as mg per l for a total pressure of 1 atm.

Figure 14 is obtained by combining Figures 12 and 13. It correlates the pressure of carbon dioxide in the vapor pressure thermometer with the moisture content of a test sample at the time of frost formation.

The expansion pressure is controlled by a simple pressure regulator or safety valve with an adjustable spring controlled by a knob and screw mechanism.

The temperature of the target is measured by means of a carbon dioxide vapor pressure thermometer. An angular-shaped cavity in the target is connected to a pressure gauge and is charged with pure carbon dioxide at room temperature at a pressure of about 160 psi. The assembly is then sealed off permanently. Care must be used in choosing a suitable ratio of target cavity volume to total volume of the thermometer system in order that the pressure gauge indicate correctly the vapor pressure of carbon dioxide in the target cavity.

The target material should be of high thermal conductivity, for example, copper, in order that the vapor pressure thermometer will give accurately the temperature of the external condensing surface. All connections to the target such as the tubular support and thermometer capillary should be of material with low thermal conductivity, for example, monel or stainless steel.

The surface of the target upon which frost is to be observed is polished and then plated with nickel or bright chromium in order to produce a flat mirror as nearly specular as possible. Small scratches or dust are confusing to the observer.

The optical system can best be described as a dark field condenser. Parallel light from a flashlight bulb and parabolic reflector enters the sample chamber through an annular Lucite window 6. The light is reflected from a conical shoulder in the sample chamber to the target surface from an oblique angle. If the target surface is a perfect mirror, all the light is reflected specularly, and none of it enters the lens tube located directly over the target. The whole interior of the sample chamber is blackened to prevent light from entering the lens tube by multiple reflections. Specks of dew or frost condensing on the target cause light to be scattered off at all angles, so that some of this light may enter the lens tube. To the observer, these specks appear as bright pin points of light in contrast to the relatively dark field.

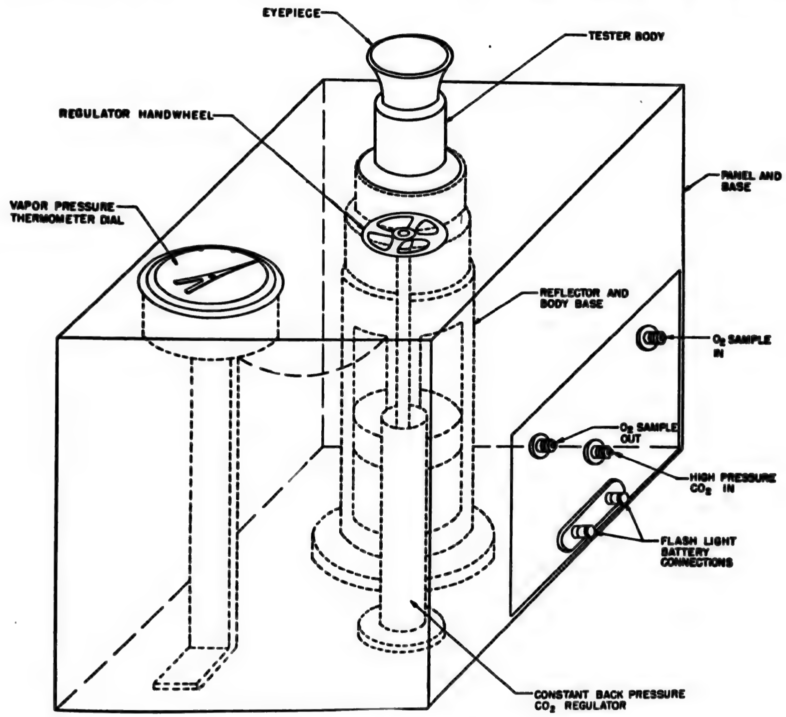


FIGURE 11. Assembly outline of McMahon dew-point apparatus.

The experimental model, with casing removed, is shown in Figure 15. In order to protect the small expansion orifice, a glass-wool filter is introduced to remove some matter from the carbon dioxide stream.

Production Models. The external appearance of the Foxboro model is shown in Figure 16. A small flow-meter has been included to adjust the flow of sample gas.

The Mine Safety Appliance model is shown in Figure 17. This instrument has been modified to include means for pressurizing the sample chamber in order to extend measurements to low moisture contents. For example, a sample of moisture content of 0.010 mg per l when pressurized to 2 atm abs will read 0.020 mg per l on the dial. In addition to a dry cell, a transformer has been included for operation of the illuminating light from a 60-cycle power line. A well at the back of the case contains a supply of tools, connection tubing, and adaptors fitting various types of carbon dioxide and oxygen cylinders.

If these instruments are to be used for the determination of moisture in carbon dioxide, a single connection to the carbon dioxide cylinder may be made

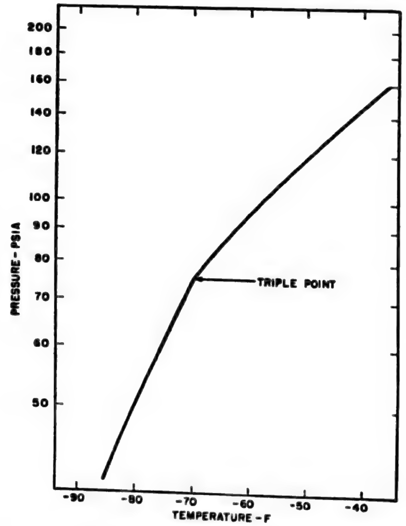


FIGURE 12. Relation of vapor pressure of CO_2 to temperature.

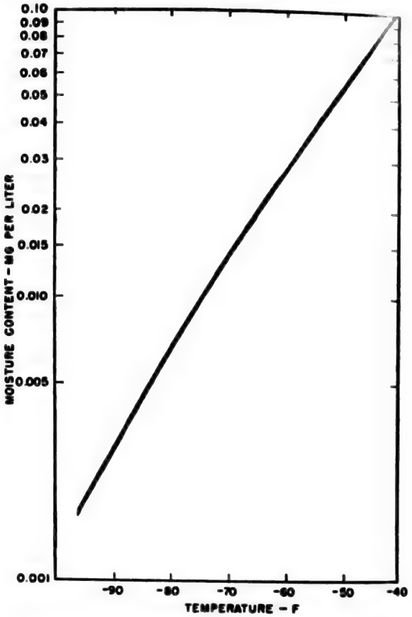


FIGURE 13. Relation of moisture content to temperature.

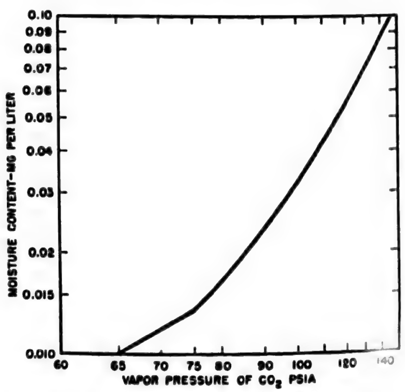


FIGURE 14. Relation of moisture content to vapor pressure of CO_2.

through a forked line, one side of which connects to the sample chamber and the other side to the refrigerating apparatus.

Operation of Instrument. Connections from carbon dioxide and oxygen cylinders are made through capillary copper tubing. It is desirable to purge the sample chamber well before releasing carbon dioxide to the refrigeration apparatus. Precautions for avoiding moisture in connections are to be observed. The initial deposit of frost near the frost point is extremely light and requires careful observation. If the frost point is to be determined accurately the measurement may be made as a series of approximations "closing in" on the actual value. The instrument is most readily used for the acceptance or rejection of gas samples at some one moisture value for which the apparatus is adjusted and observance made for the absence or presence of deposits upon the target.

Various forms of the apparatus described above, with careful manipulation, have given results accurately to $\pm$ 0.003 mg per l when the mirror surface of the target is excellent. Even with a poor mirror surface and clumsy manipulation an accuracy of $\pm$ 0.01 mg per l is possible. A common source of error is the presence of a number of condensable gases or other impurity in the vapor pressure thermometer.

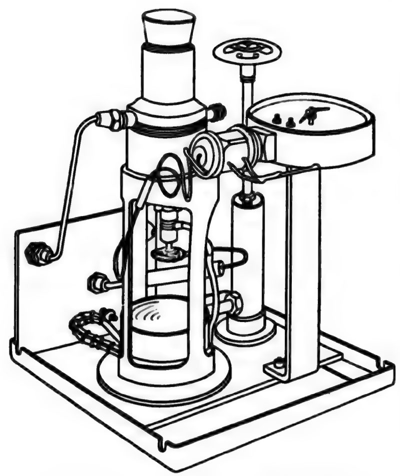


FIGURE 15. McMahon dew-point apparatus.

Suggested Modifications and Further Research. The target and optical system of experimental models have not been perfected; improvement will lead to much greater accuracy and ease of determinations. Modifications and adaptation of other frost-point

FIGURE 16. Foxboro type apparatus for determining moisture in aviator's oxygen.

FIGURE 17. Mine Safety type water vapor indicator.

ranges may be made by substituting other condensable gases in the vapor pressure thermometer and adjusting the carbon dioxide regulator.

14.4 INSTRUMENT FOR DETERMINING A COMBINATION OF PROPERTIES OF COMPRESSED OXYGEN GAS

A cabinet-style water-vapor indicator of the electrical conductivity type,[22] manufactured by the American Instrument Company, was altered by rearrangement of valves and connecting tubing to permit installation of a Model P Pauling oxygen meter[4] within the cabinet and upon the instrument panel of the water-vapor indicator.[*] A sensitive pressure regulator was installed between the oxygen sample line of the water-vapor indicator and the Pauling oxygen meter to prevent damage to the latter. In addition, an exhaust of the oxygen sample line is provided with a connection for carbon monoxide test ampules developed by the National Bureau of Standards.

It is, therefore, possible, with a single connection to an oxygen cylinder, to determine the cylinder pressure and moisture content (water vapor indicator), the partial pressure or percentage of oxygen (Pauling oxygen meter) and the concentration of carbon monoxide and certain other impurities, by the insertion of suitable ampules in the sample exhaust connection.

14.5 COMBINED VAPOR-PRESSURE AND GAS THERMOMETER

In connection with the operation of the oxygen generating units described in earlier chapters, it was believed desirable to develop simple, rugged thermometers which would be sensitive to 1 F over the entire working range, or roughly from —320 F to +150 F. A combined vapor-pressure and gas thermometer filled with oxygen or nitrogen seemed ideal for this purpose.

The thermometer[10,11,12] comprises a Bourdon-type pressure gauge, a bulb, and flexible, armored capillary tubing connecting the gauge and bulb. In order to insure accuracy as a gas thermometer, the gas volume of the Bourdon tube and the capillary tubing should be small relative to the volume of the bulb. Specifications are:

1. Bulb. ¼-in. OD, 0.035-in. wall, copper tubing 10 in. long, welded shut at one end and fitted at the other end with a plug drilled to fit the connecting capillary tubing.
2. Connecting tubing. Twelve ft of copper capillary with a volume of 0.064 ml per ft. It is covered with a flexible stainless steel protecting armor.
3. Gauge. The gauge has the usual Bourdon tube and gear arrangement; Bourdon tubes of small volume are to be preferred. The dial of the gauge was graduated in degrees Fahrenheit as determined by calibration against a thermocouple and certain fixed points such as the boiling point of oxygen, ice point, etc. A sample calibration curve is given in Figure 18.
4. The thermometer is filled with pure oxygen or pure nitrogen to a predetermined pressure while the temperature of the bulb is held at a predetermined value.

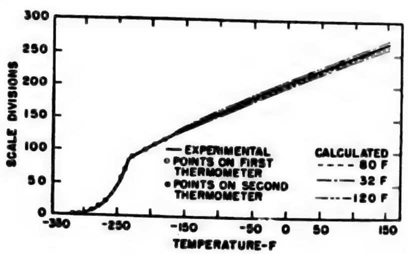


FIGURE 18. Scale divisions vs temperature for oxygen and nitrogen thermometers.

The Tagliabue Manufacturing Company of Brooklyn, New York, has worked out production methods for this thermometer which avoid the necessity for individual calibration.[10]

14.6 A DIAL-TYPE LIQUID LEVEL GAUGE

The standard manometer type of liquid level gauge in common use on stationary liquid oxygen plants to indicate the height of liquid at the bottom of the fractionating column, is not suitable for use on portable generators because of its fragility and danger of spilling. The following differential pressure gauge was, therefore, developed for use on portable liquid oxygen generators.[16]

A sensitive double diaphragm similar to that employed in the anneroid barometer, and a rack and pinion mechanism for translating the motion of the diaphragm into the rotation of a pointer spindle were enclosed in a gas-tight case provided with a pressure resistant dial glass. The case is provided with a lead for attachment to the lesser of the two pressures whose difference it is desired to measure. The connection to the interior of the diaphragm was used for the greater of the two pressures. The case of the meter was built to withstand the operating pressure of the rectification column.

[*] The structural changes in the instruments were very kindly made by the National Bureau of Standards under the supervision of Dr. E. R. Weaver. Dr. Weaver and his associates also contributed many valuable suggestions to the construction and operation of this and other water-vapor indicators which they tested.

Chapter 15

SUBMARINE PROBLEMS

By *S. S. Prentiss*[a]

15.1 INTRODUCTION

The fact that there were certain undesirable limits of speed and cruising radius placed on submarines dependent on storage batteries for submerged propulsion prompted a study of operation of diesel and other combustion engines with combustion-supporting secondary fuels. NDRC undertook a threefold program which included (1) the generation of large amounts of oxygen aboard submarines while surfaced, for use as secondary fuel while submerged, see Chapters 3 and 4, (2) the operation of diesel engines under submerged conditions, and (3) the disposal of exhaust gases from submerged submarines to minimize the chances of enemy detection. Auxiliary problems which later developed included the supply of oxygen and the removal of carbon dioxide from the atmosphere within submarines to permit long periods of submersion.

15.2 OPERATION OF DIESEL ENGINES WHILE SUBMERGED (RECYCLED EXHAUST GASES)

As a first approach to the propulsion of submerged submarines, it was proposed to use the diesel engines normally used for surface propulsion. A program was therefore undertaken to demonstrate the feasibility of operating diesel engines under conditions approximating those of a submerged submarine and to develop the optimum conditions for such operation. Such a program was carried out on small experimental diesel engines with satisfactory results.

15.2.1 Problems of Recycle Operation

In order to prevent overloading and overheating of the diesel engine when operating on oxygen it is necessary to recycle exhaust gases as a diluent for the working fluid. (See Figure 1.) Since this exhaust gas (water vapor and carbon dioxide) has a higher heat capacity than nitrogen, which is the oxygen diluent for air, the theoretical efficiency of an engine operating on recycle cannot be greater than 87% of that obtained with air for the same compression ratio. In addition, ignition delay is appreciably greater than on air.

Disposal of fixed gases presents a major problem in the underwater operation of diesel engines using "oxygen-recycle." For this reason and for economy of secondary fuel, it is desirable to reduce the oxygen in the waste exhaust gases to as small a quantity as possible. The problem of oxygen disposal in the exhaust from the two-cycle engine, which requires excess working fluid for scavenging, appeared to be more acute than with the four-cycle engine. In addition to the above, engine noise (knocking) under most conditions of operation was greater than on air.

15.2.2 Apparatus and Materials

The tests were made, employing two different single-cylinder diesel engines and one 6-cylinder automotive type diesel, as described in Table 1.

Table 1

	General Motors Model 1-71	Waukesha CFR	Hercules Model DJXB
Power	15 hp @ 1200 rpm	...	77 hp @ 2600 rpm
Type	2 cycle with built-in blower-direct injection	4 cycle with comet-type antechamber	4 cycle, with Hercules turbulence combustion chamber (automotive type)
Size	4¼ x 5, single cylinder	3¼ x 4½, single cylinder	3¾ x 4½, 6 cylinder
Compression ratio	16 to 1	15.5 to 1	16 to 1
Injection equipment	GM standard unit injector	Bosch fuel pump and injector	Bosch fuel pump and injectors

The engine was directly connected to a cradle-type electric dynamometer for measuring power. Temperatures, pressures, flow rates, gas composition, et cetera, were determined with regular laboratory instruments and standard test procedures. Ignition delay was obtained with a Sunbury cathode-ray type engine indicator.

[a] Technical Aide, Division 11, NDRC.

All tests were made with commercial diesel fuel having the following specifications.

Gravity, API	37.0
Cetane No., ASTM	51
Viscosity @ 100 F, SSU	35
Mid-boiling point, F	504
Final boiling point, F	640

15.2.3 Experimental Procedure

The test procedure used conformed to the regular accepted standards covering the type of operation involved. In Table 2 are presented the principal operating conditions used for recycle operation.

Table 2

	General Motors Model 1-71	Waukesha CFR	Hercules Model DJXB
Speed, rpm	900 and 1200	950	1200
Load	½ to full	Various	½ to full
Temperature F, working fluid to engine	250	250	250
Temperature F, oil	180	150	170
Temperature F, water out	180	212	170
Back pressure, in. of Hg	0.5 (normally)	0.1 (normally)	0.5
Fuel injection angle-degree	14 BTDC		14 BTDC

15.2.4 Results and Conclusions

No special problems were encountered in operating the test engines on oxygen recycle within the range of one-half to full rated power. All the test work proceeded without incident. It was found, however, that to avoid the possibility of an explosion it was advisable to keep the oxygen concentration at the engine intake below 50%.

Under regular recycle operation for the various test engines, oxygen loss varied from 10 to 17% at full load to 25 to 35% at approximately one-half load (see Figure 2). In attempts to reduce this loss the waste exhaust gas from the larger GM engine was fed to the smaller CFR engine (see Figure 3). In this type of series operation the overall oxygen loss was reduced to 4%. In further tests, water scrubbing of the exhaust gas was employed and by this method oxygen losses were reduced to 2% (see Figure 4). Using this system and feeding oxygen containing 5% argon increased engine efficiencies over those obtained with 100% oxygen feed and reduced the noise level to at least that obtained with air (see Figure 5). However, the water and power requirements necessary for this type of operation may be prohibitive.

It was concluded from these tests that oxygen recycle operation of diesel engines is feasible and that sufficient data are available[2] to be able to set

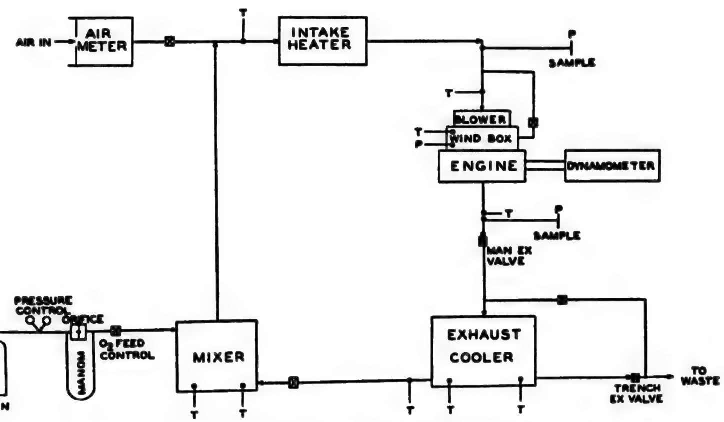


Figure 1. Schematic diagram of test setup of 1 cylinder 2 cycle GM diesel engine.

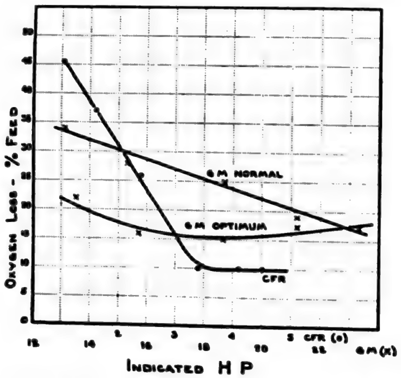


FIGURE 2. Oxygen recycle tests of 1 cylinder GM and CFR diesels. Per cent O_2 lost at various loads.

down and compare the various methods of operation from the standpoint of equipment and power requirements to enable an approximation of the optimum method of operation. The whole program, however, was abruptly terminated when the Navy decided that the operation of submarines by diesel engines was not permissible because of the high noise level.

15.3 DISPOSAL OF ENGINE EXHAUST WHILE SUBMERGED

15.3.1 Jet Dispersion into Sea

An important auxiliary problem to the operation of diesel engines aboard submerged submarines was the disposal of exhaust gas therefrom in such a manner as not to add to the visibility of the submarine from air reconnaissance. The problem was never clearly defined as the definite restriction of visibility to overhead observation; it was interpreted, therefore, as one of dispersing the gas into the sea in the form of bubbles sufficiently small as to be completely absorbed while rising toward the surface, from a minimum or critical depth of 30 ft. The possibilities of the gas cloud dispersal method are illustrated in Figure 6.

The plan proposed for full-scale operation involved internal combustion engines to produce about 2,700 indicated horsepower and 188 lb moles per hr of hot raw exhaust gas consisting of 86.7 lb moles per hr of water vapor (1,560 lb of steam), 86.7 lb moles per hr of carbon dioxide (3,800 lb), and 15.3 lb moles per hr of oxygen and argon. On the dry basis, the dehumidified exhaust gas would then contain 85% carbon dioxide by volume and 15% oxygen and argon. A study of gas cloud solution in sea water

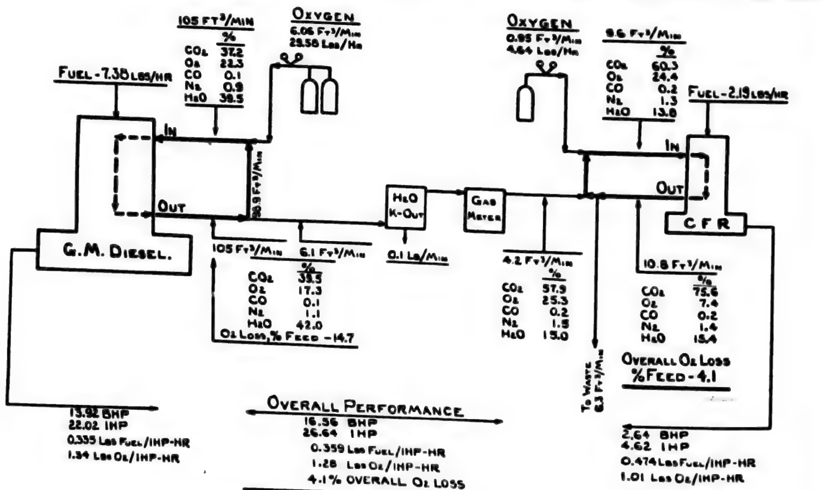


FIGURE 3. Series operation of 2 cycle GM and 4 cycle CFR diesels. Oxygen recycle operation.

was made with bubbles of various controlled sizes. The bubble of critical or maximum diameter that will dissolve from a given depth with exhaust gases of different composition are shown in Figure 7.

A series of tests was made on a small scale in a vertical glass column and later repeated in Boston harbor (see Figure 8 and Figure 9). For dispersing the gas, injectors were found to be more economical of power than porous plates. A two-stage water injector is more economical than a single stage, as shown in Figure 10. For a constant total outlet and arrangement of the holes in the final disperser, a large number of holes is economical on total power and water; however, nozzles of diameters less than 0.3 in. are not recommended because of the possibility of clogging. Details of experimental nozzles are shown in Figures 11 and 12.

The experimental results may be summarized in the following application to a submarine diesel engine developing 2,700 hp.[1] When operating 110 of the recommended dispersers in parallel to share the full-scale gas rate, at a depth of 30 ft, the necessary water pump would handle 1,500 gal per min and develop a pressure difference of 62 psi, consuming 54 theoretical hp. If the total dry gas from the dehumidifier (657 cu ft per min at 1 atm abs and 70 F) is compressed isothermally from atmospheric pressure to the pressure at the inlet to the dispersers (58 psi gauge) 67 theoretical hp are required. The total power for both gas and water is then 121 theoretical hp, or 155 shaft hp with 83% efficiency for the water pump and 75% efficiency for the gas compressor. The total shaft hp required is then 5.8% of the 2,700 indicated hp developed by the internal combustion engines producing the gas which contains 3,800 lb/hr of carbon dioxide and enough oxygen and argon to give a mixture containing 85% carbon dioxide by volume. The velocity of the water, through the nozzle in the injector, would be approximately 26 miles per hr and the velocity of the mixture of water and gas (assuming water and gas volumes are additive at the outlet of the disperser at 30 ft depth) would be 74 mph.

15.3.2 Sea Water Scrubbing

A superficial investigation was made of apparatus for scrubbing exhaust gases with sea water inside of the pressure hull. The prohibitive size of the equipment for completely dissolving the exhaust gases in sea water within the pressure hull caused this method to be discarded in favor of the method of dispersing exhaust gases into the sea.

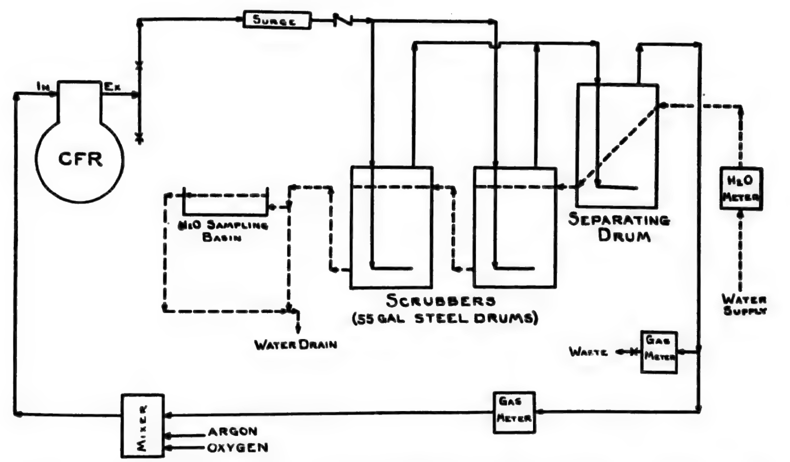


FIGURE 4. Oxygen recycle operation of 1 cylinder CFR diesel engine with argon using exhaust gas scrubbing.

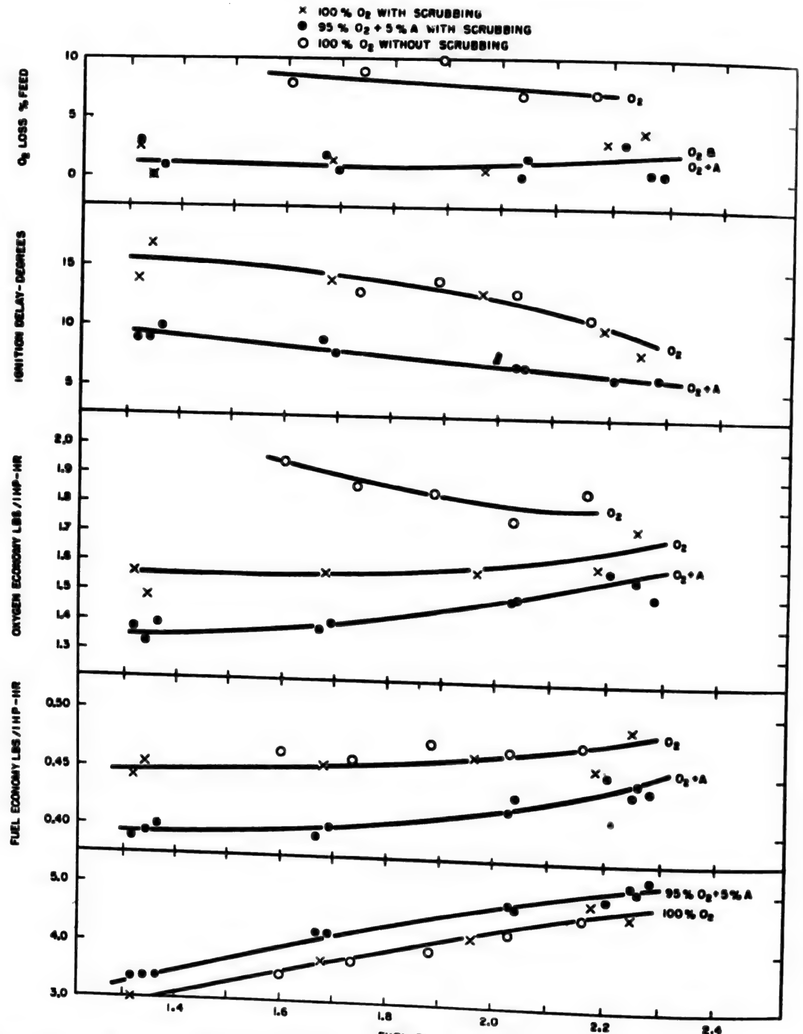


FIGURE 5. CFR diesel-recycle operation. Performance curves using 100% O_2 and 95% O_2 + 5% A with H_2O scrubbing, and 100% O_2 without scrubbing.

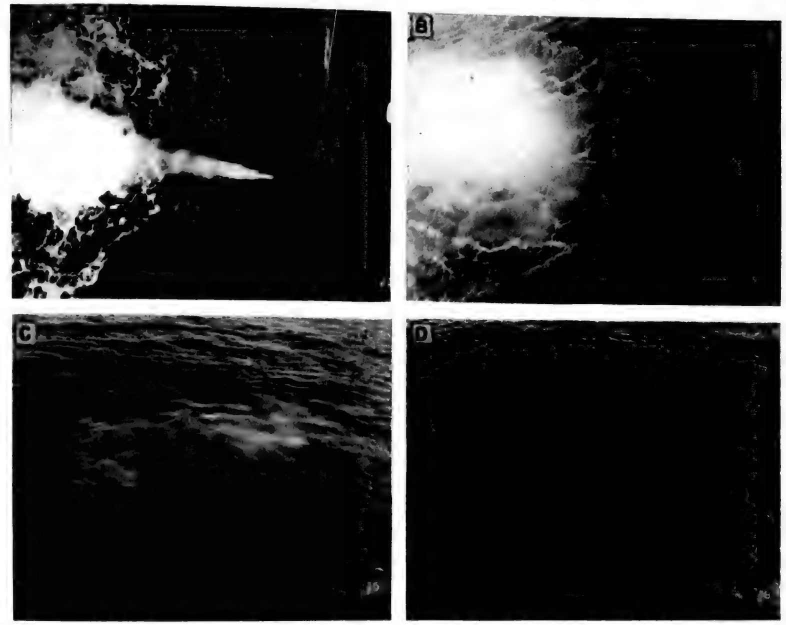


FIGURE 6. Exhaust gas cloud dispersal at various depths.

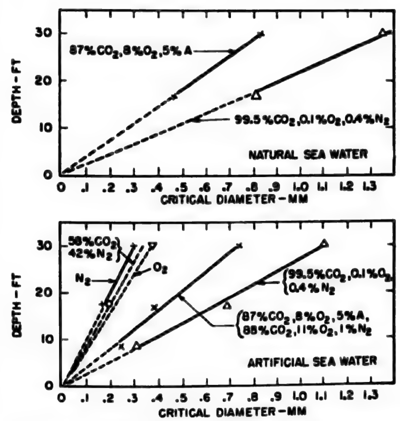


FIGURE 7. Effect of depth on critical diameter of gas bubbles in (1) natural and (2) artificial sea water.

15.3.3 Recommendations for Future Research

The operation of other forms of internal combustion power mechanisms (for example, gas turbines) on recycled gases should be studied. The substitution of other power source in the submarine may eliminate objections to noise, et cetera. Means for entirely eliminating exhaust gases within the hull should be developed along the lines set forth under "Air Conditioning." This may be practical for low-power (50 to 100 hp) and thus reduce the hazards of detection when the submarine is "lying low."

15.4 AIR CONDITIONING

The long periods of submergence indicated by the foregoing form of propulsion made it desirable to provide means for maintaining breathing standards in the submarine atmosphere for long periods of time, preferably indefinitely. Table 3 presents a comparison of methods for maintaining normal atmospheric conditions on a submarine.

TABLE 3.* Comparison of estimated volumes and weights of present and proposed chemical and mechanical methods for maintaining normal atmospheric conditions on a submarine; (calculations based on 60-man submarine crew) (volume in cu ft and weights in lb).

Basis for calculations	Present method ($LiOH$ & O_2) Volume	Weight	KOX or MOX canisters Volume	Weight	Chlorate candles and LiOH Volume	Weight	Keyes unit and CO_2 sea water scrubbing Volume	Weight	Stored liquid O_2 and CO_2 sea water scrubbing Volume	Weight
75 hr CO_2 absorbing 18 hr O_2 available										
Canisters	15.0	525	45.0	2,421	15.0	525	‡0.15	18		
Candles					2.7	279	23.0			
Cylinders	14.0	700								
Mechanical							23.0	X	23.0	X
apparatus			†		3.0	84	17.0	X	5.0	X
Total	29.0	1,225	45.0	2,421	20.7	888	40.15	X	28.0	X
75 hr CO_2 absorbing 75 hr O_2 available										
Canisters	15.0	525	45.0	2,421	15.0	525	‡0.6	75		
Candles					11.3	1,170				
Cylinders	64.4	3,220								
Mechanical							23.0	X	23.0	X
apparatus			†		3.0	84	17.0	X	20.0	X
Total	79.4	3,745	45.0	2,421	29.3	1,779	40.6	X	43.0	X
300 hr CO_2 absorbing 300 hr O_2 available										
Canisters	60.0	2,100	180.0	9,684	60.0	2,100	‡2.4	300*		
Candles					44.7	4,680				
Cylinders	252.0	12,600								
Mechanical							23.0	X	23.0	X
apparatus			†		3.0	84	17.0	X	75.0	X
Total	312.0	14,700	180.0	9,684	107.7	6,864	42.4	X	98.0	X

X Data lacking.
* Ref: Research Memorandum No. 2-44 NAVSHIPS (330), March 21, 1944.
† Assumes use of portable blowers now on submarines.
‡ Not canisters but KOH containers.

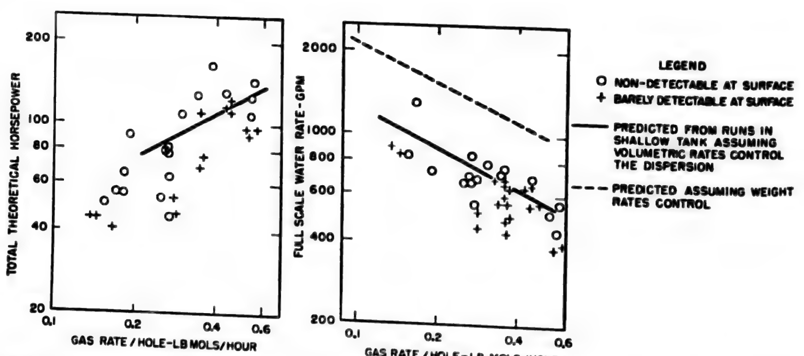


FIGURE 8. Navy Yard runs. Dispersion of 85% CO_2—15% O_2 in 30 feet of salt water. Disperser: Type R with Richards Pump. Observations in bright sunlight.

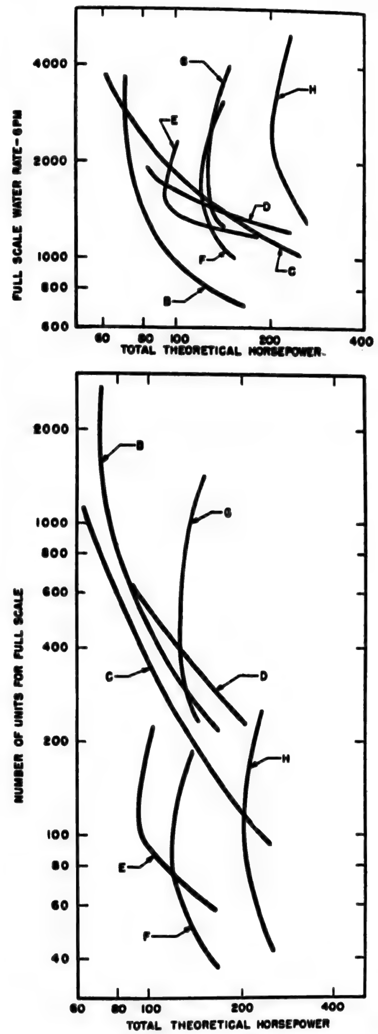


FIGURE 9. Requirements for complete absorption of 85% CO_2—15% O_2 mixture in 30 feet of sea water.

15.4.1 **Supply of Oxygen**

Of the methods of supplying oxygen for breathing purposes on a submarine, NDRC contributed only the development of a generator for separating atmospheric oxygen. This is a compact unit operating with one torpedo-charging air compressor and producing approximately 20 lb of liquid oxygen per hr while the submarine is surfaced. This liquid oxygen can then be slowly evaporated while the submarine is submerged and thus replenish the oxygen supply.

15.4.2 **Removal of Carbon Dioxide**

The results of a survey of methods of absorbing carbon dioxide are summarized in Table 4.[2] Two of these methods were selected for experimental evaluation, and full sized units were built for demonstration purposes.

The first of the methods developed was scrubbing with sea water as shown in the flow sheet, Figure 13.[3,4,5,6] The unit operated with an absorption tower 5 ft high, packed with 1-in. Raschig rings. The absorption tower was operated at a relatively high pressure, that is, the ambient pressure of the sea, which varies with the depth of submergence. The air was compressed to the operating pressure of the tower, scrubbed with sea water, and then expanded into the hull of the submarine. Inasmuch as some cooling takes place, the operation of the unit may lead

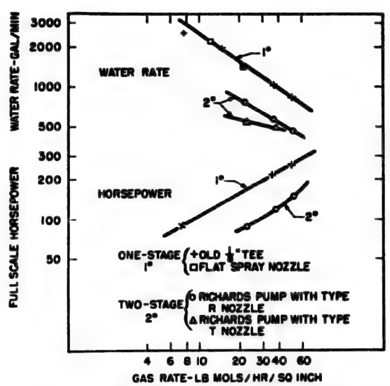


FIGURE 10. Critical tank data—0.85 mm bubble. Calculated for full scale operation comparing one and two stage dispersers.

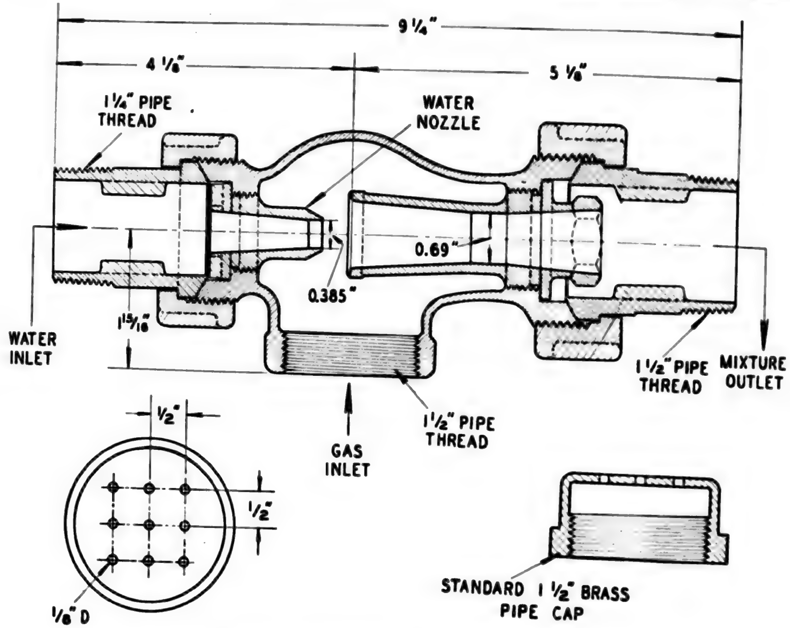


FIGURE 11. Hancock ejector with water nozzle.

to a reduction in the operation of other air conditioning systems on the submarine. In another form of the apparatus, a jet-absorption unit is substituted for the packed tower, with a consequent reduction in the size of the equipment (see Figure 14).

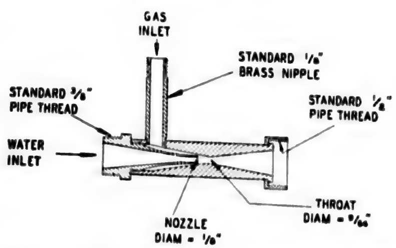


FIGURE 12. Brass Richards pump used in series with Sprayco nozzle in two-stage dispersal.

A second form of apparatus[3,4,5,6] employs ethanolamine as the scrubbing agent as shown in Figure 15. This system has the advantage that it may be completely contained in the hull of a submarine and therefore may be operated at the pressure of the submarine atmosphere. A suitable proportion of the atmosphere of the submarine may be circulated through the ethanolamine absorption tower and returned to the submarine atmosphere. The carbon dioxide is then desorbed from the ethanolamine and pumped overboard into the sea or compressed into pressure vessels.

15.4.3

Recommendations for Future Research

The apparatus developed so far is a first attempt. There should be opportunity for reducing the size and power requirements of this equipment by investigation and development of absorption equipment.

TABLE 4. Summary of pertinent facts about processes for carbon dioxide removal from air in submarines.

Process	Estimated volume cu ft	Estimated power hp	Process oxygen required, lb per hr	Remarks
1a. Refrigeration with liquid O_2	Not estimated	Negligible	28	In addition to high oxygen there is uncertainty about CO_2 deposition which will necessitate considerable development.
1b. Refrigeration with liquid O_2 and Freon	Not estimated	3	15	Same as for 1a.
1c. Same as (1b) plus recovery of latent heat of condensation of CO_2	Up to 165	7–15	5	The uncertainty regarding the CO_2 deposition will mean considerable development. Most of the volume is that of the vacuum pump; this might be reduced by changes in process.
1d. Refrigeration by expander	Not estimated	18	0	In addition to high-power requirement process will require considerable development.
2a. Adsorption, low pressure, O_2 refrigeration	Not estimated	Negligible	28	In addition to the high O_2 requirement this process would require considerable development.
2b. Same as (2a) but with Freon refrigeration	195	7	0	Requires considerable development. Hopeful, however, because CO_2 deposition less uncertain than in process 1. Most of the volume is that of the vacuum pump; this might be reduced by changes in process.
2c. Intermediate pressure; expander refrigeration	Not estimated	18	0	In addition to higher power, would require considerable development.
2d. High pressure adsorption	30	17	0	Assumes compressor already available. Untried and would need considerable development.
3a. Sea water scrubbing—1 atm	75	10–50	0	Power varies with depth. Power is chiefly to pump water out. A simple process requiring little development.
3b. Sea water scrubbing—50 lbs per sq in.	31	6–11	1.2 (2/1 lb N_2)	Power varies with depth. A simple process requiring little development.
3c. Sea water scrubbing at sea pressure	32	4–10	0.8–1.0 (1.4/1.8 lb N_2)	Power varies with depth. Power chiefly for air compression. A simple process requiring little development.
4. Scrubbing with Amine	14	0.5 for mechanical power. 9.5 for heat	0	Similar processes in use so little development required.
5a. Absorption by LiOH	62	Negligible	0	This is good for only 320 hours. Volume is that for storage of chemical.
5b. Absorption by K_2O_4	180	Negligible	0	This supplies necessary oxygen. Remarks under (5a) also apply. Chemical is hazardous.

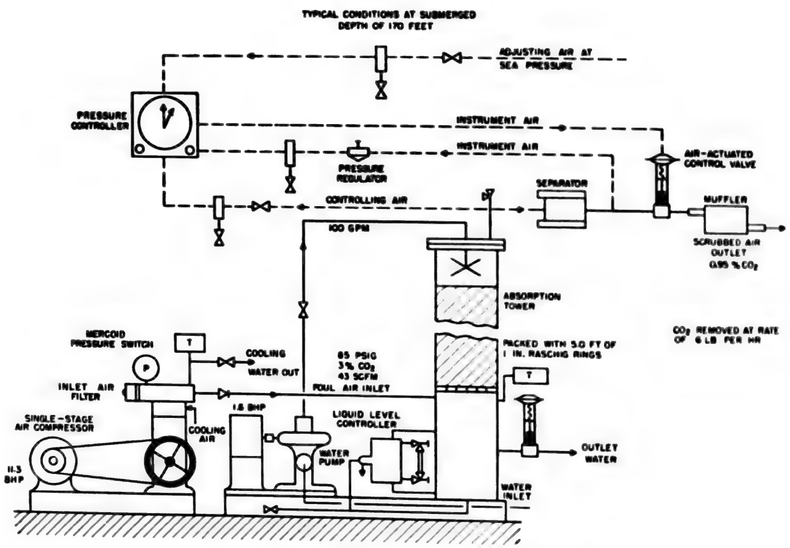


FIGURE 13. Sea water pilot plant demonstration unit.

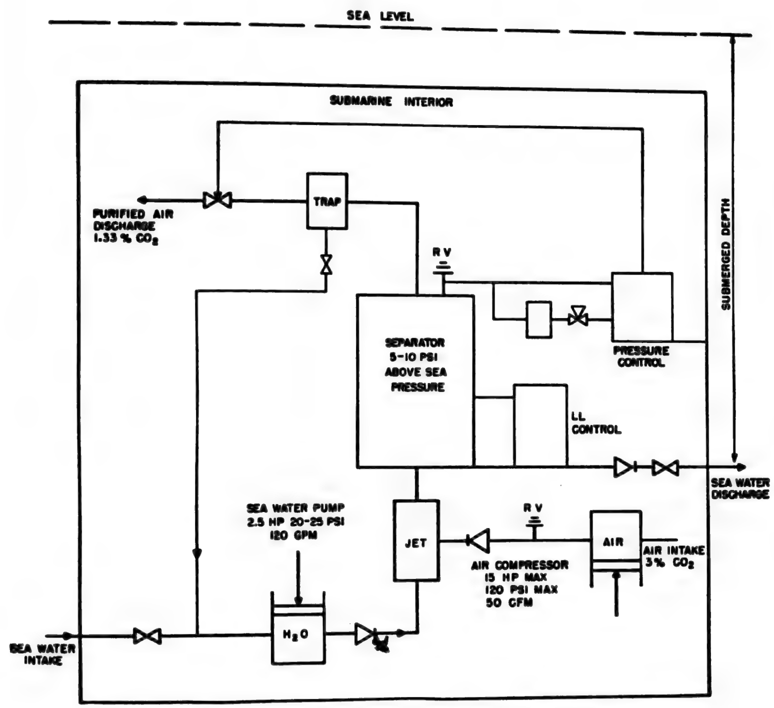


FIGURE 14. Schematic diagram of jet-type air scrubber unit installed in submarine.

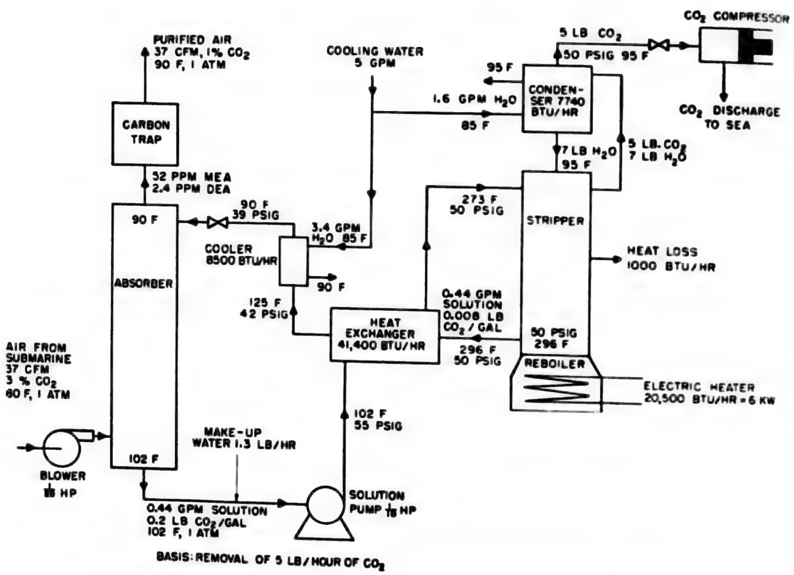
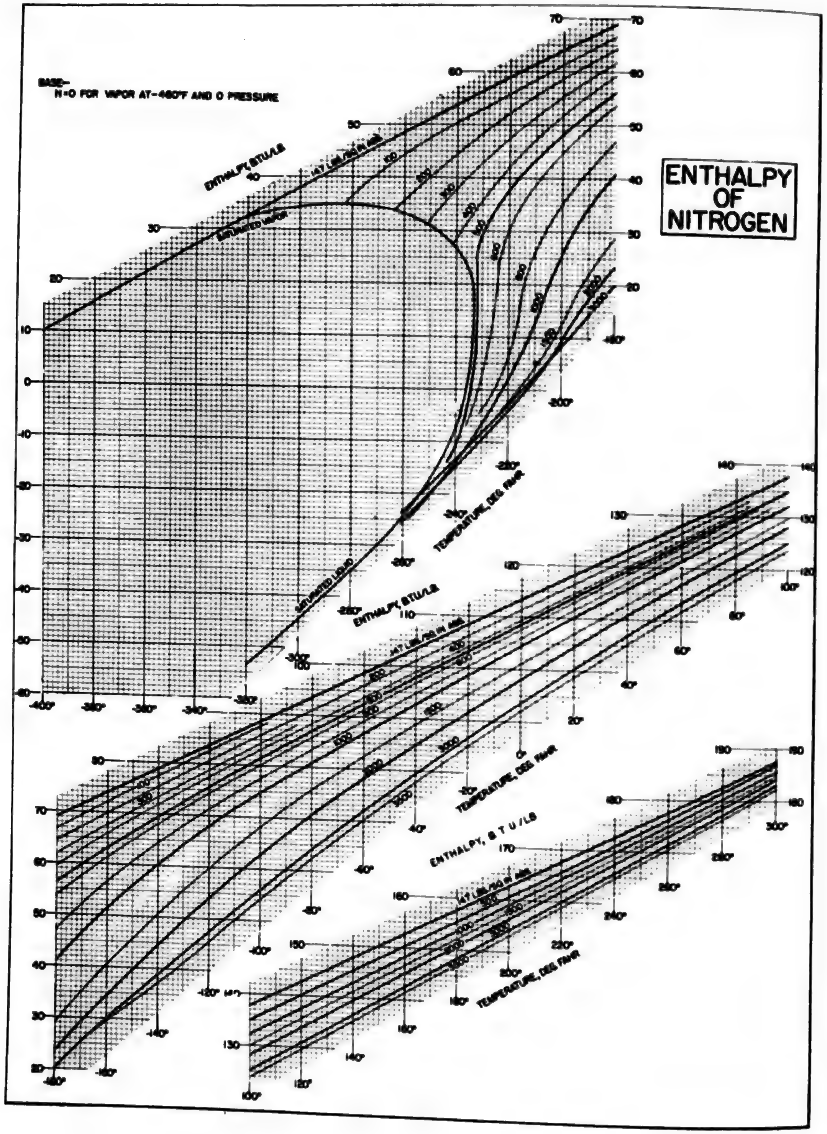


FIGURE 15. Process flow sheet of S-2 unit. CO_2 removal by ethanolamine scrubbing.

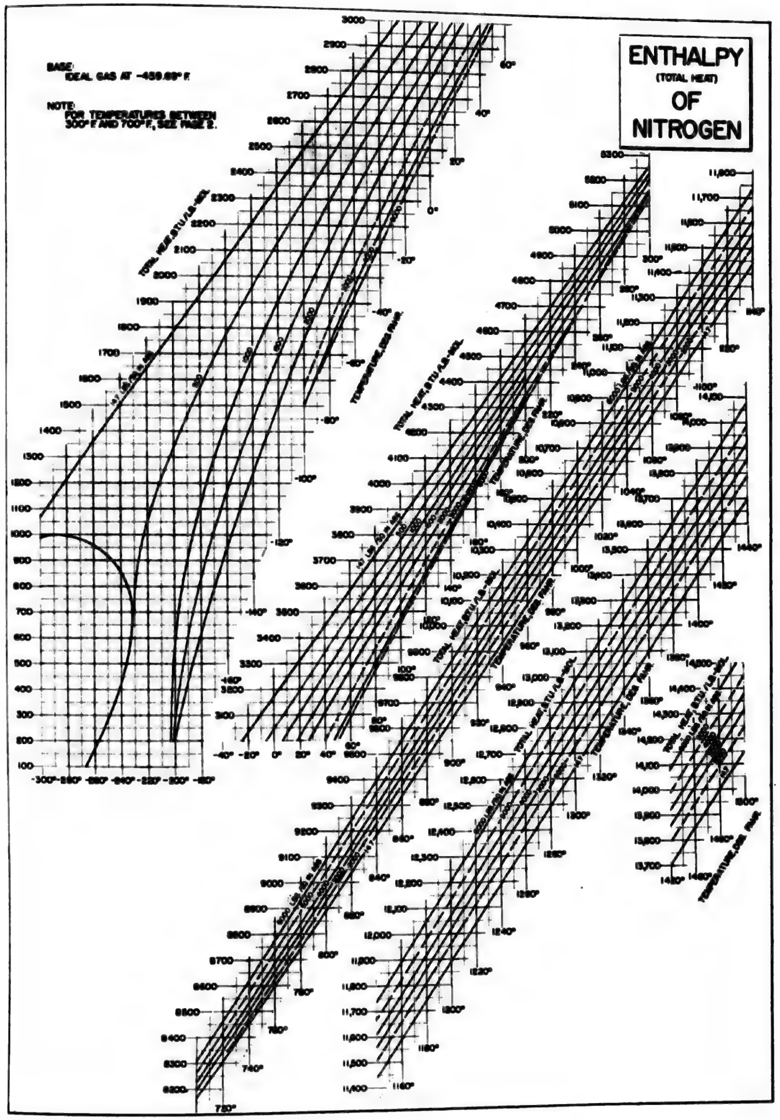
APPENDIX A

DATA ON AIR AND ITS COMPONENTS

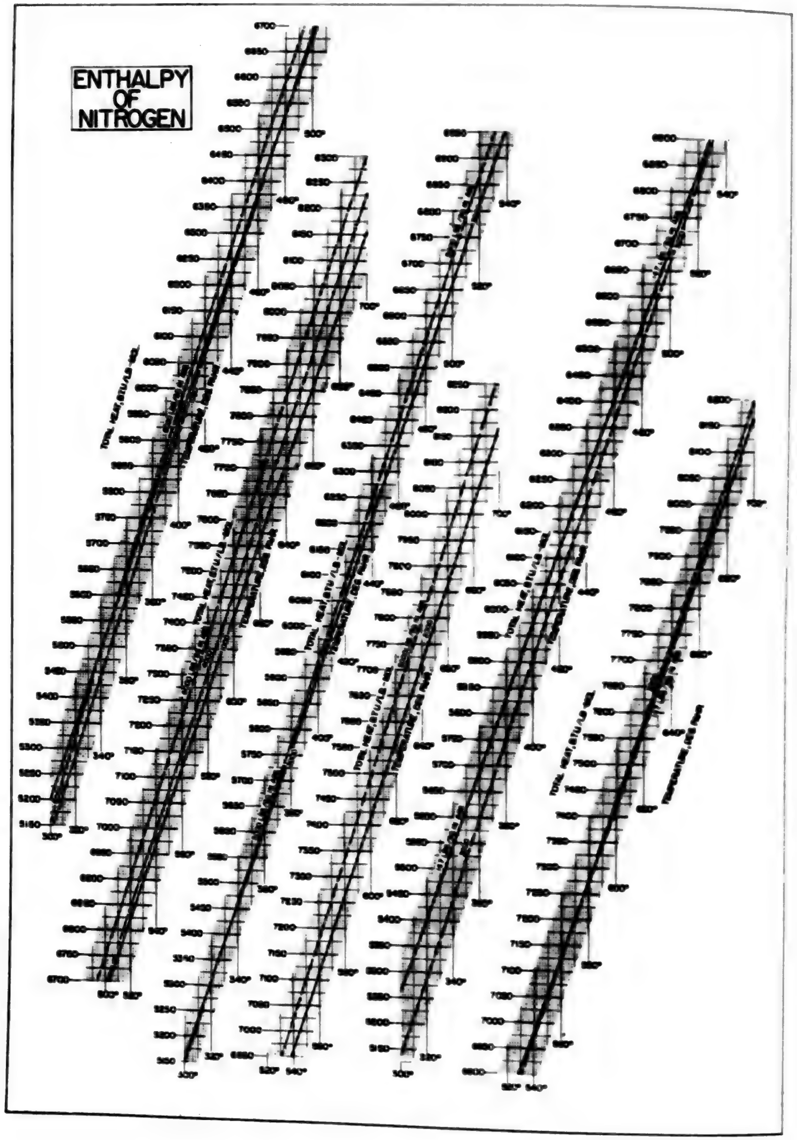
Data	Curve Number
Nitrogen	
Enthalpy (for temperatures below 0° F)	G-602.301
Enthalpy	G-602.31
Vapor pressure	G-602.51
Density of gaseous nitrogen, lb/cu ft	G-602.60
Temperature entropy diagram	G-602.65
Temperature entropy diagram	G-602.66
Temperature entropy diagram	G-602.67
Thermal conductivity	G-602.80
Viscosity	G-602.90
Argon	
Enthalpy	G-603.30
Vapor pressure	G-603.50
Density	G-603.60
Thermal conductivity	G-603.80
Viscosity	G-603.90
Oxygen	
Enthalpy	G-605.30
Vapor pressure	G-605.50
Density	G-605.60
Temperature entropy diagram	G-605.65
Temperature entropy diagram	G-605.66
Thermal conductivity	G-605.80
Viscosity	G-605.90
Helium	
Enthalpy	G-609.30
Temperature entropy diagram	G-609.65
Carbon Dioxide	
Enthalpy	G-675.30
Vapor pressure	G-675.51
Density	G-675.60
Temperature entropy diagram	G-675.65
Thermal conductivity	G-675.80
Viscosity	G-675.90
Air	
Enthalpy	G-815.30
Enthalpy of oxygen-nitrogen mixtures at 14.7 psia	G-815.31
Enthalpy of oxygen-nitrogen mixtures at 75 psia	G-815.32
Enthalpy of oxygen-nitrogen mixtures at 150 psia	G-815.33
Enthalpy entropy diagram of air	G-815.34
Vapor pressure of liquid oxygen and nitrogen mixtures	G-815.50
Dew-point pressures of gaseous oxygen-nitrogen mixtures	G-815.51
Equilibrium of oxygen-nitrogen mixtures	G-815.52
Equilibrium of nitrogen-argon mixtures	G-815.53
Equilibrium of oxygen-argon mixtures	G-815.54
Liquid-vapor equilibrium for oxygen-nitrogen system	G-815.56
Density of air	G-815.60
Temperature entropy diagram for air	G-815.65
Temperature entropy diagram of air	G-815.66
Thermal conductivity of air	G-815.80
Viscosity of air	G-815.90
Viscosity of liquid nitrogen-oxygen mixtures	G-815.91

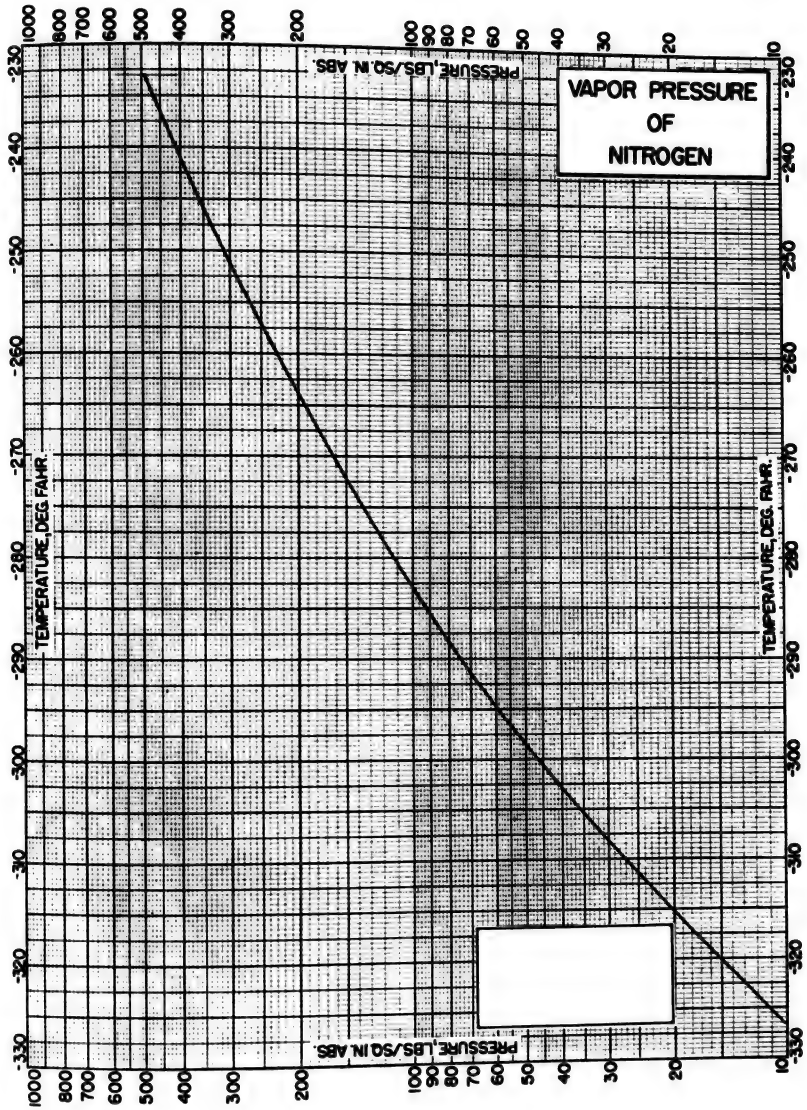


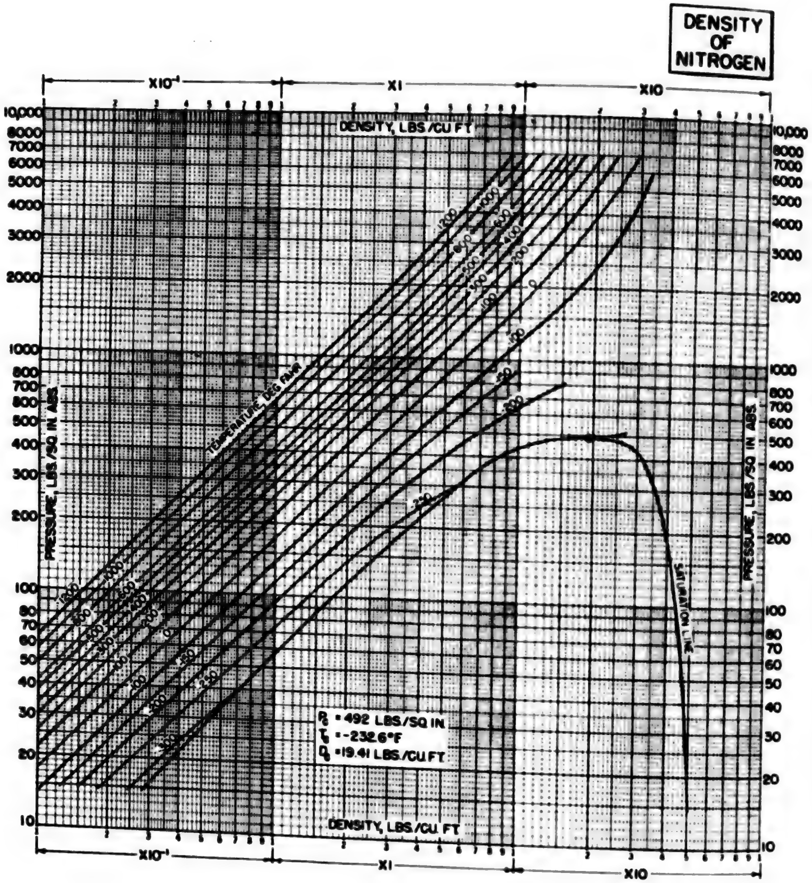
G-602.301

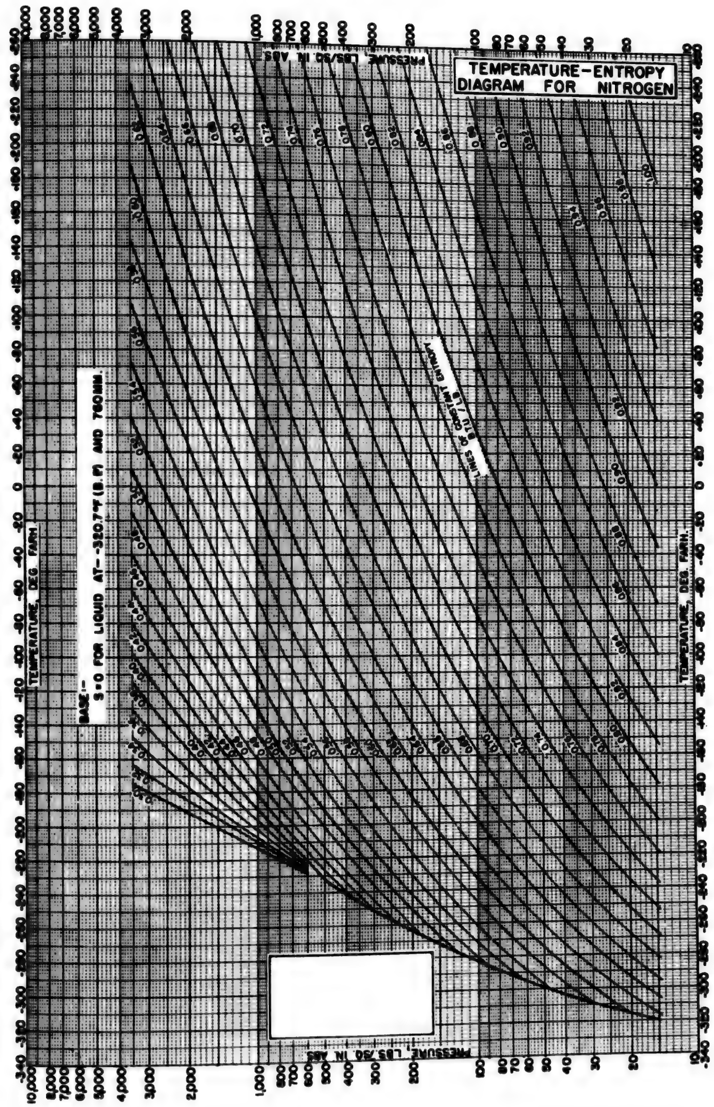


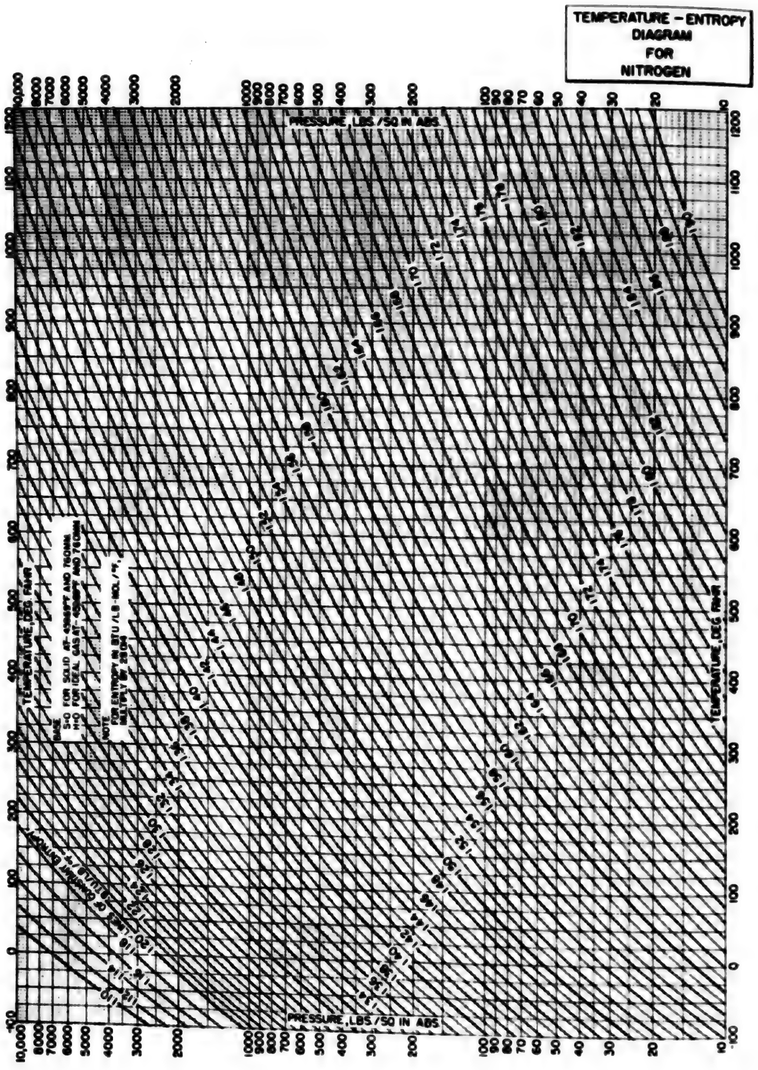
G-602.31—Part 1


ENTHALPY
OF
NITROGEN

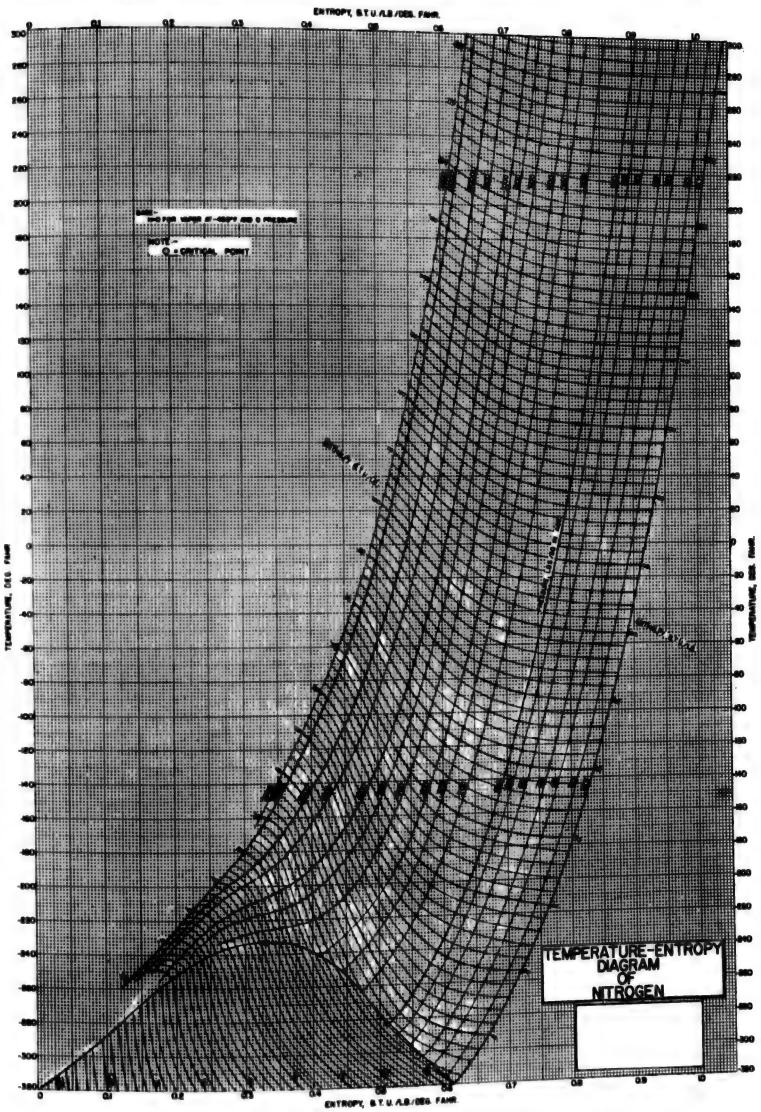

VAPOR PRESSURE
OF
NITROGEN
PRESSURE, LBS/SQ.IN. ABS.
TEMPERATURE, DEG. FAHR.
1000
800
700
600
500
400
300
200
100
90
80
70
60
50
40
30
20
10
-230
-240
-250
-260
-270
-280
-290
-300
-310
-320
-330


DENSITY OF NITROGEN
DENSITY, LBS/CU FT
PRESSURE, LBS/SQ IN ABS
TEMPERATURE, DEG FAHR
SATURATION LINE
P_c = 492 LBS/SQ IN
T_c = -232.6°F
D_c = 19.41 LBS/CU FT

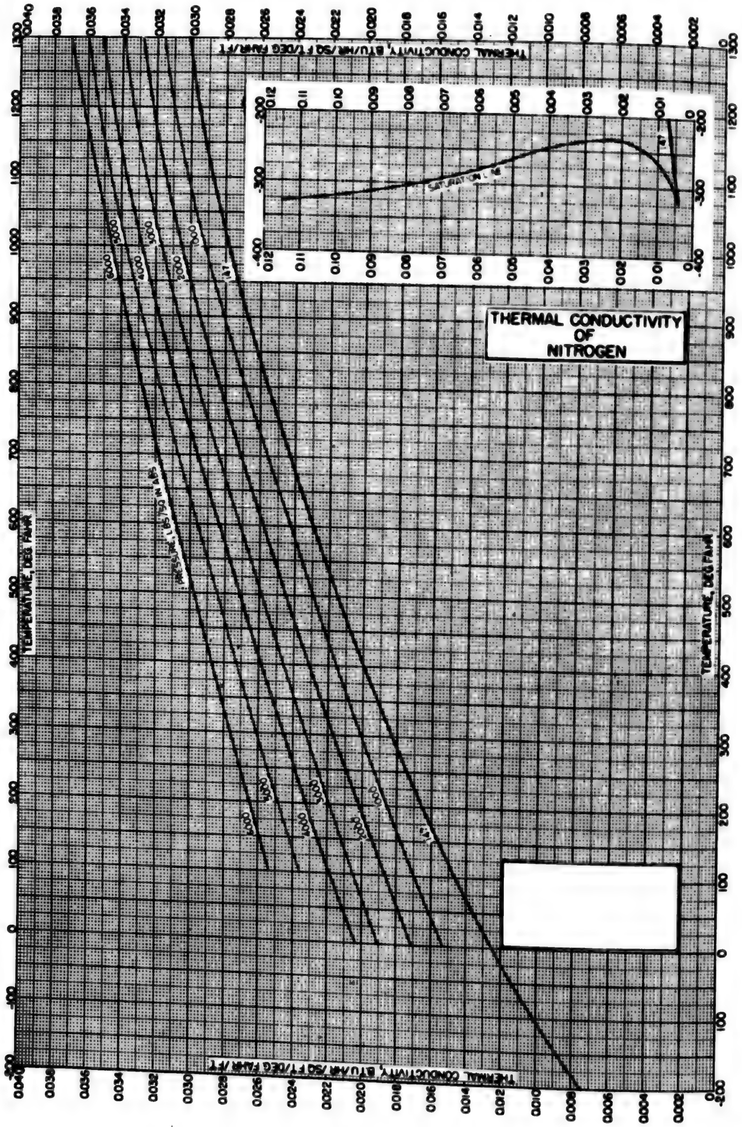

TEMPERATURE-ENTROPY DIAGRAM FOR NITROGEN
LINES OF CONSTANT ENTROPY BTU / LB
BASE:- S=0 FOR LIQUID AT -320.7°F (B.P.) AND 760MM.
TEMPERATURE, DEG FAHR
PRESSURE, LBS/SQ IN ABS



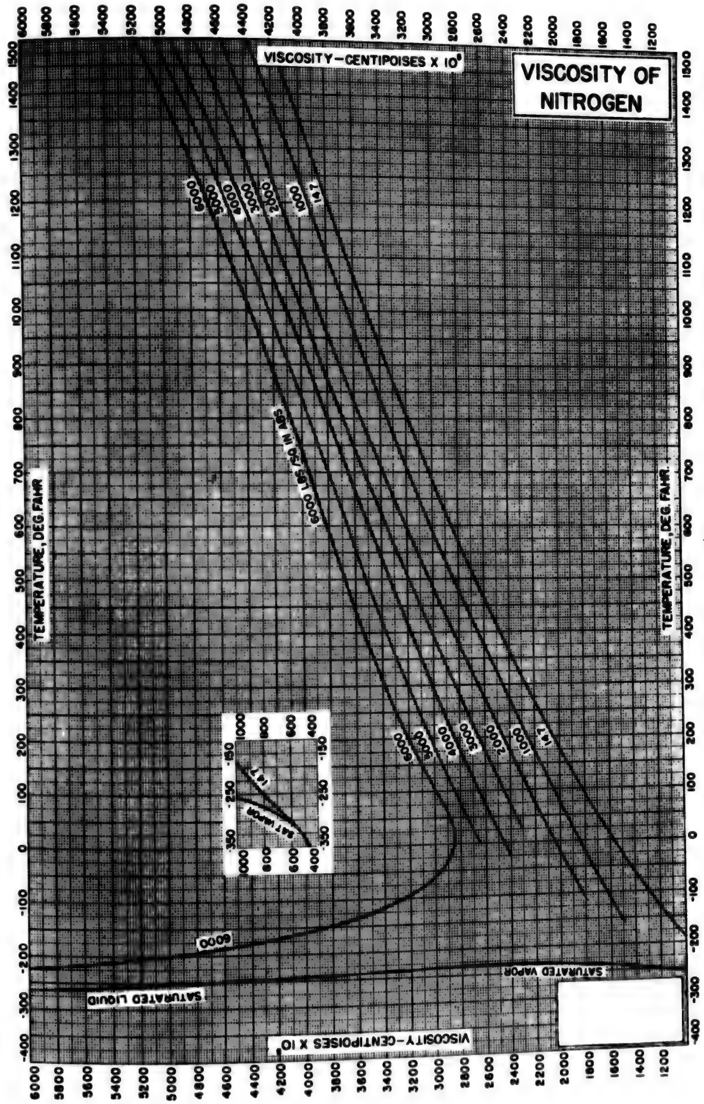
G-602.66



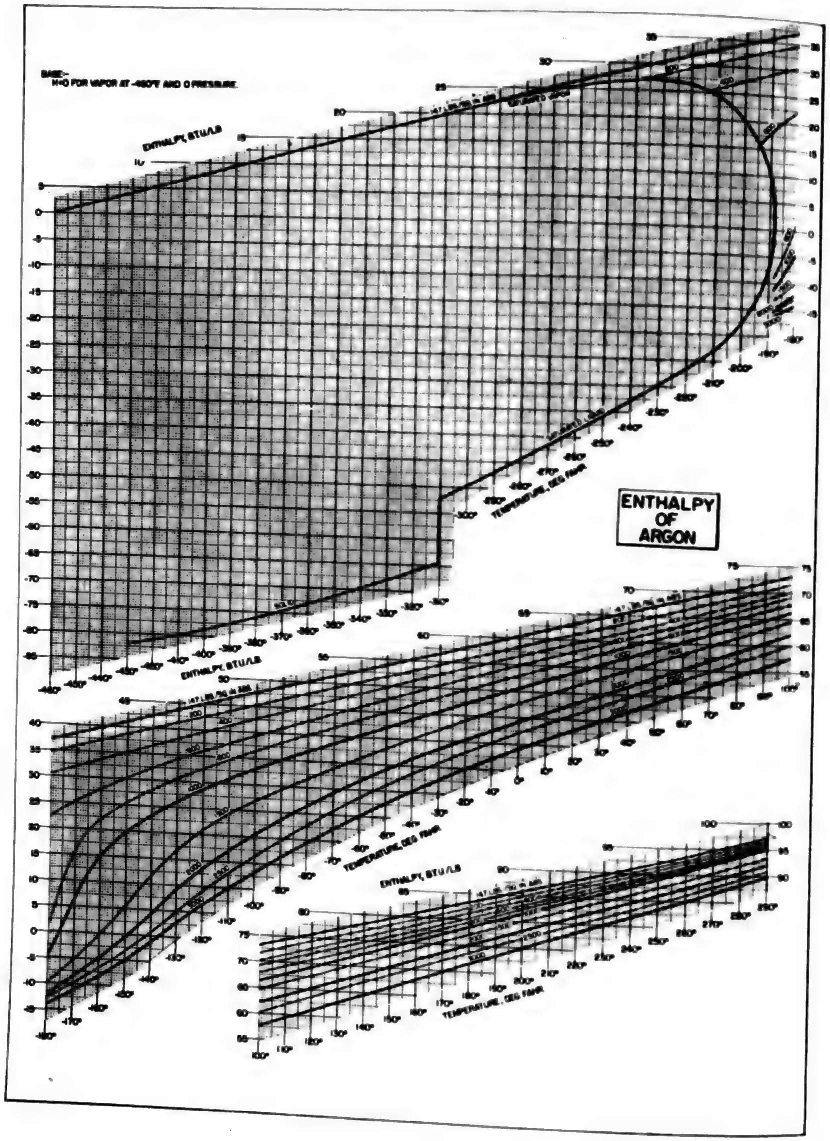
G-602.67



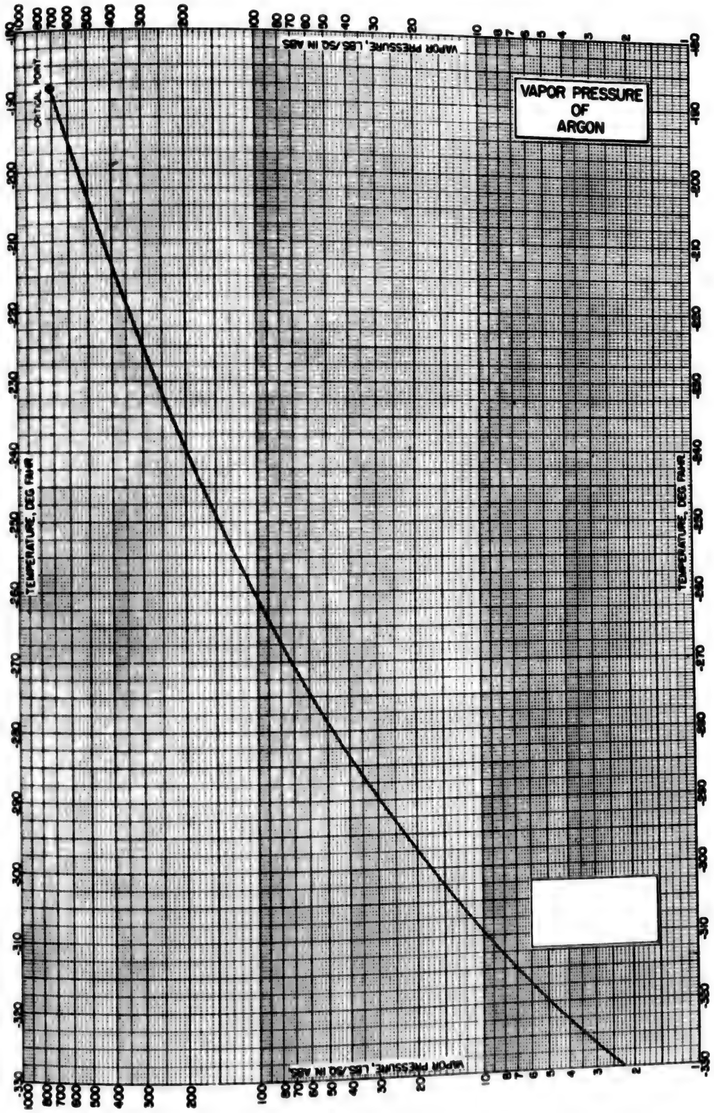
G-602.80



G-602.90

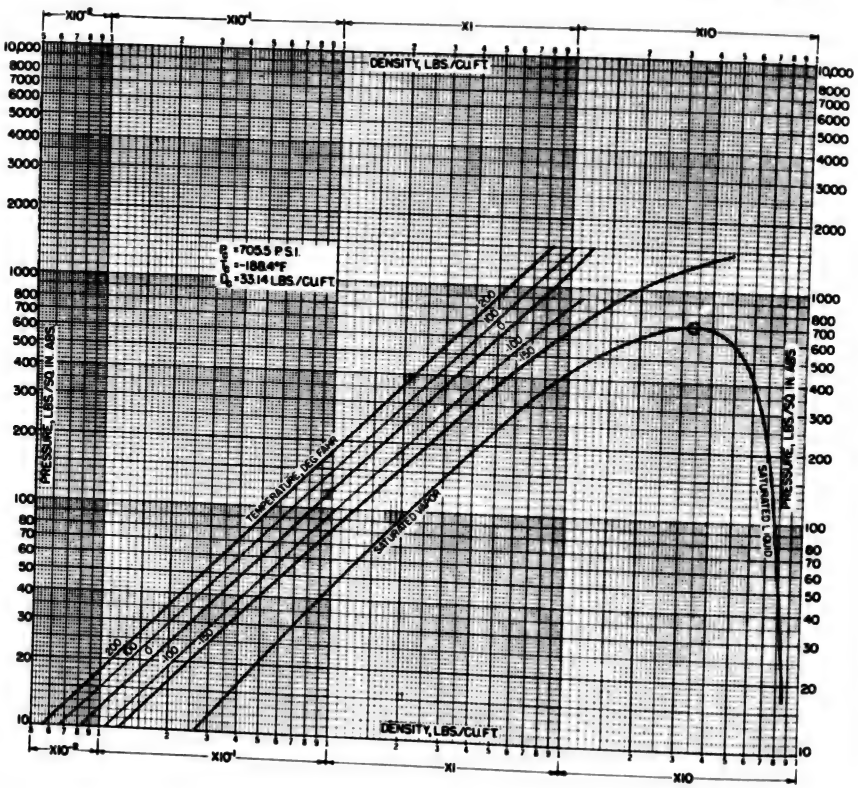


G-603.30

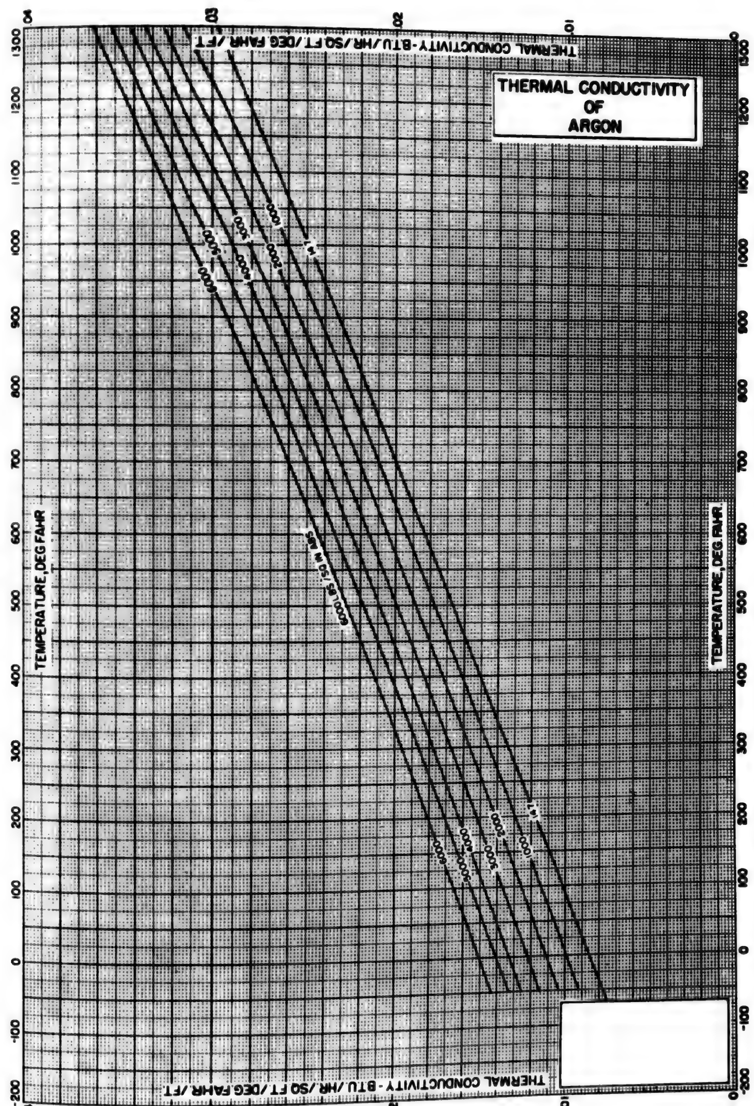


G-603.50

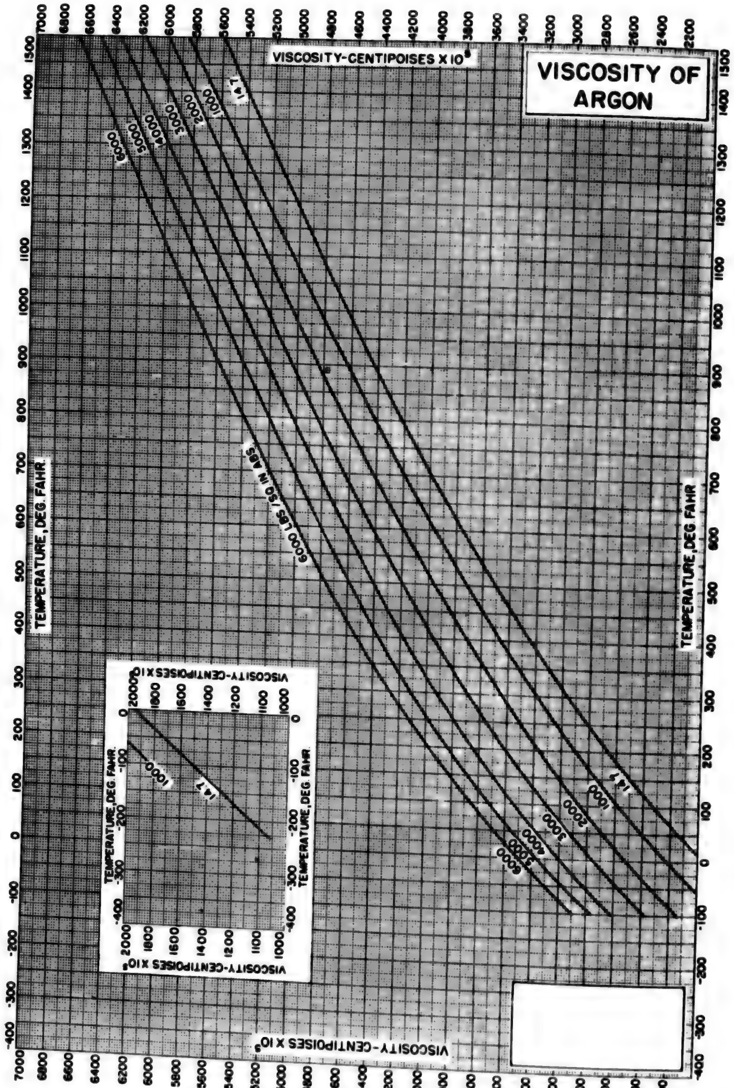
DENSITY OF ARGON

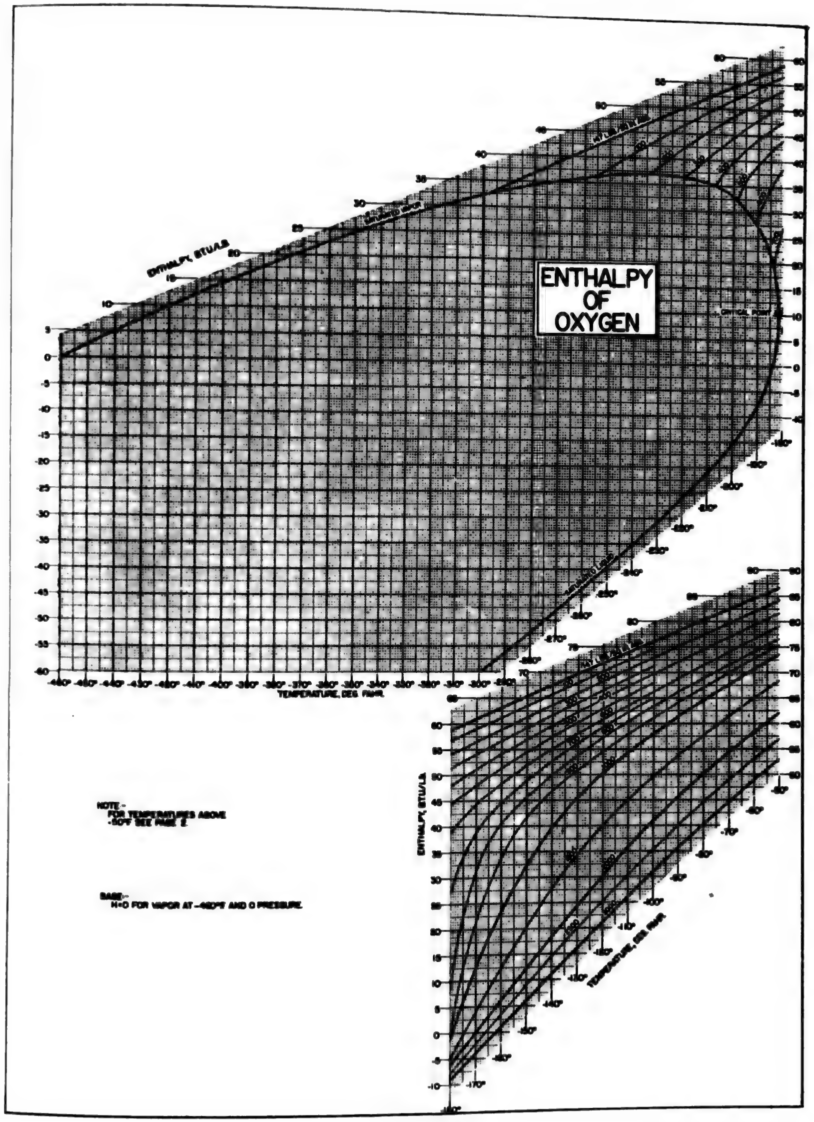


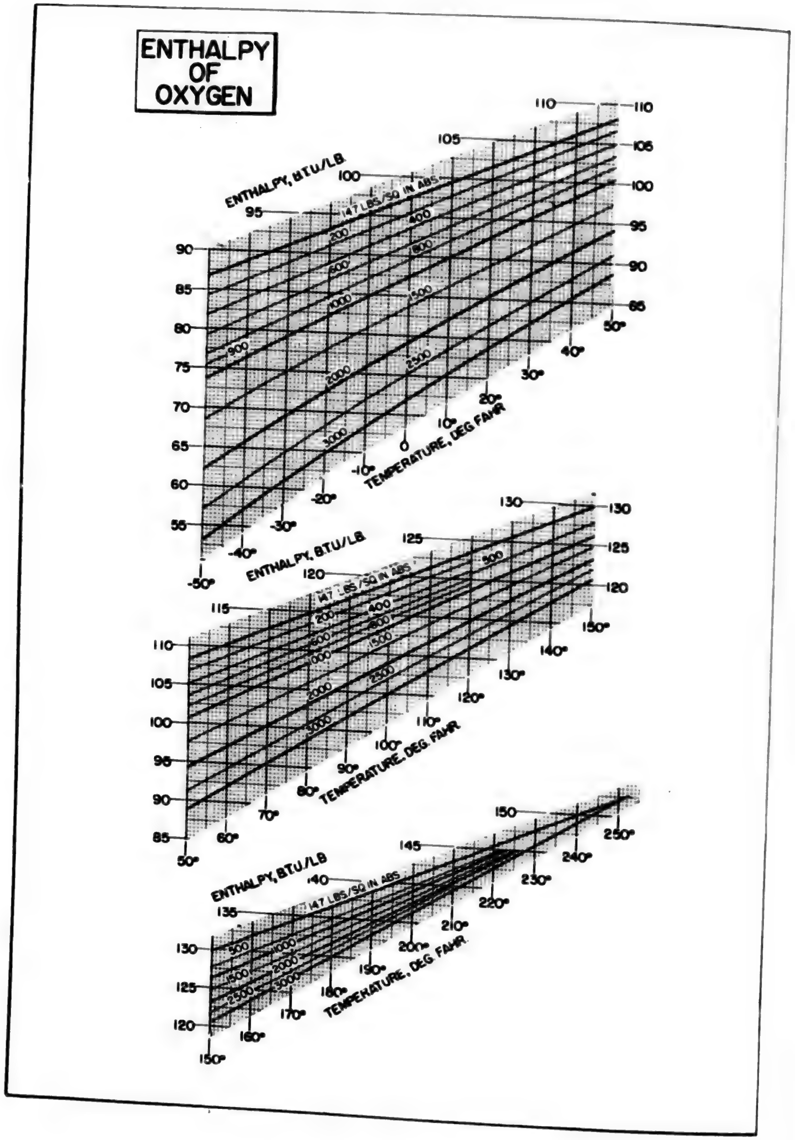
G-603.60



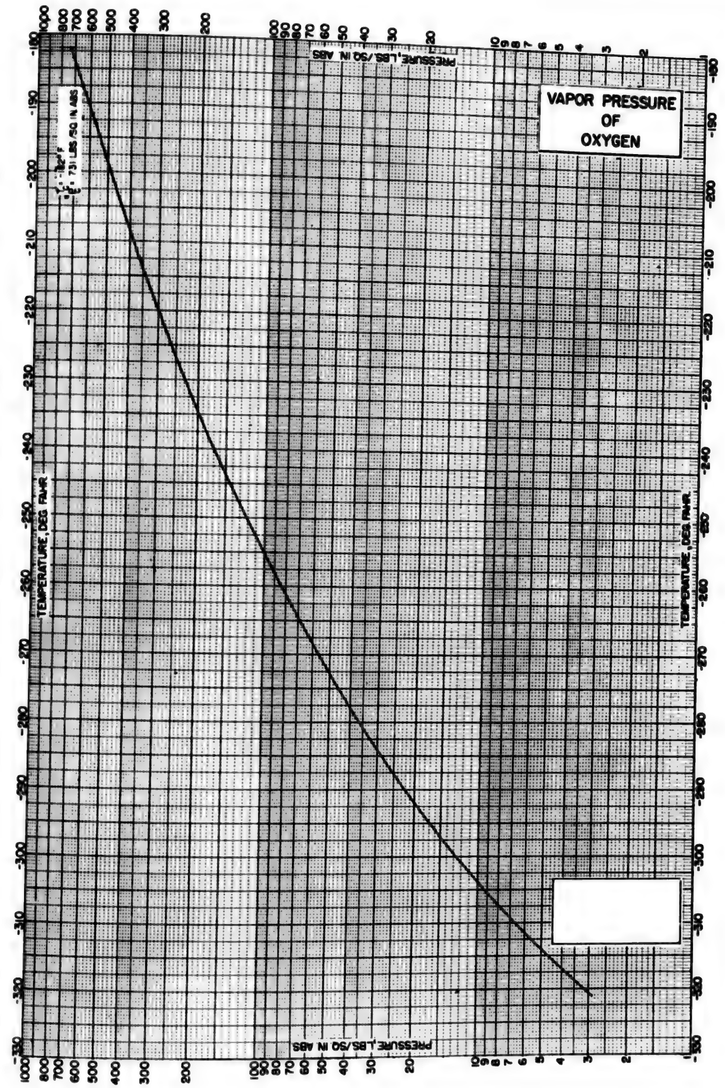
G-603.80


VISCOSITY OF ARGON
VISCOSITY-CENTIPOISES X 10^8
TEMPERATURE, DEG. FAHR.
6000 LBS./SQ. IN. ABS.
14.7
1000
2000
3000
4000
5000
6000

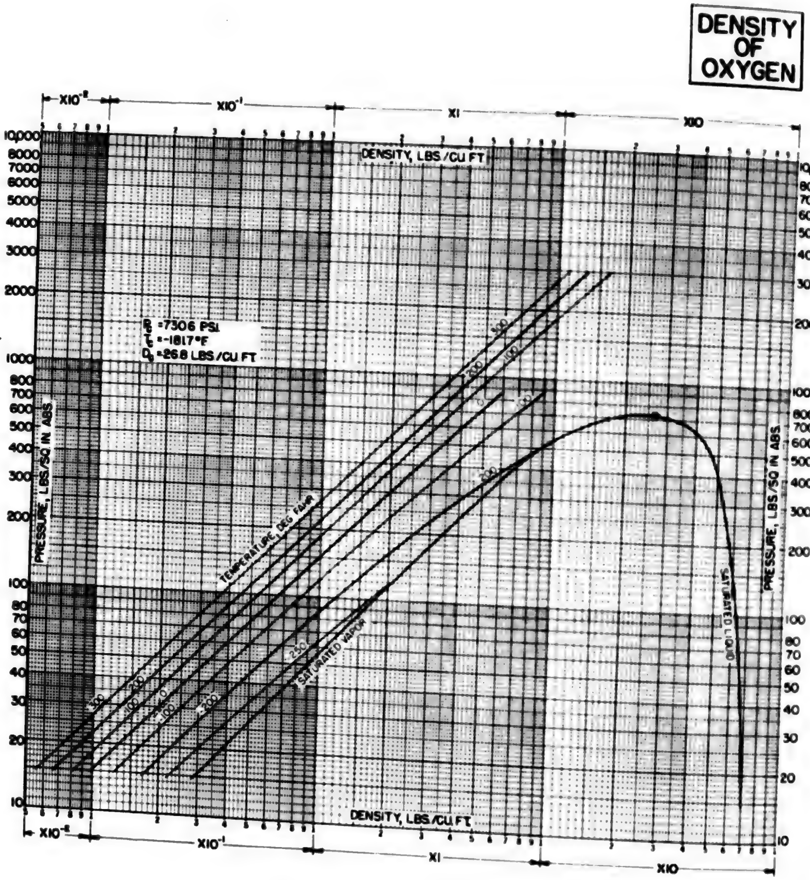

ENTHALPY OF OXYGEN
ENTHALPY, BTU/LB.
TEMPERATURE, DEG. FAHR.
NOTE—
FOR TEMPERATURES ABOVE
-50°F SEE PAGE 2
BASE—
H=O FOR VAPOR AT -460°F AND O PRESSURE



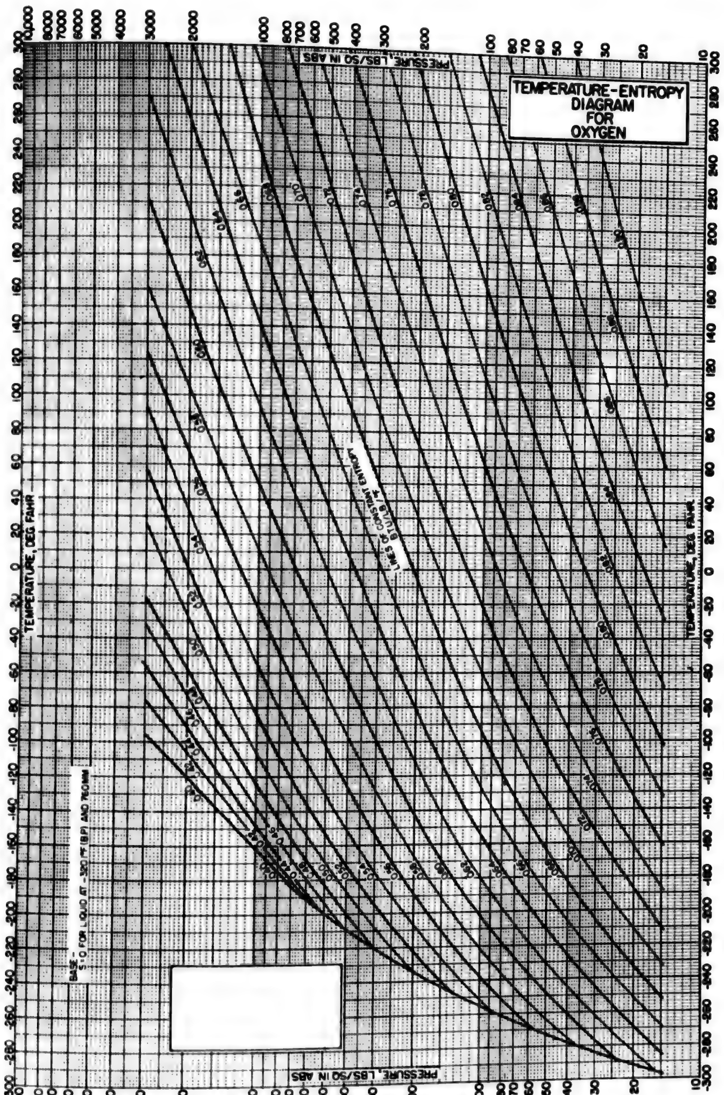
ENTHALPY
OF
OXYGEN
ENTHALPY, BTU/LB
TEMPERATURE, DEG FAHR
147 LBS/SQ IN ABS



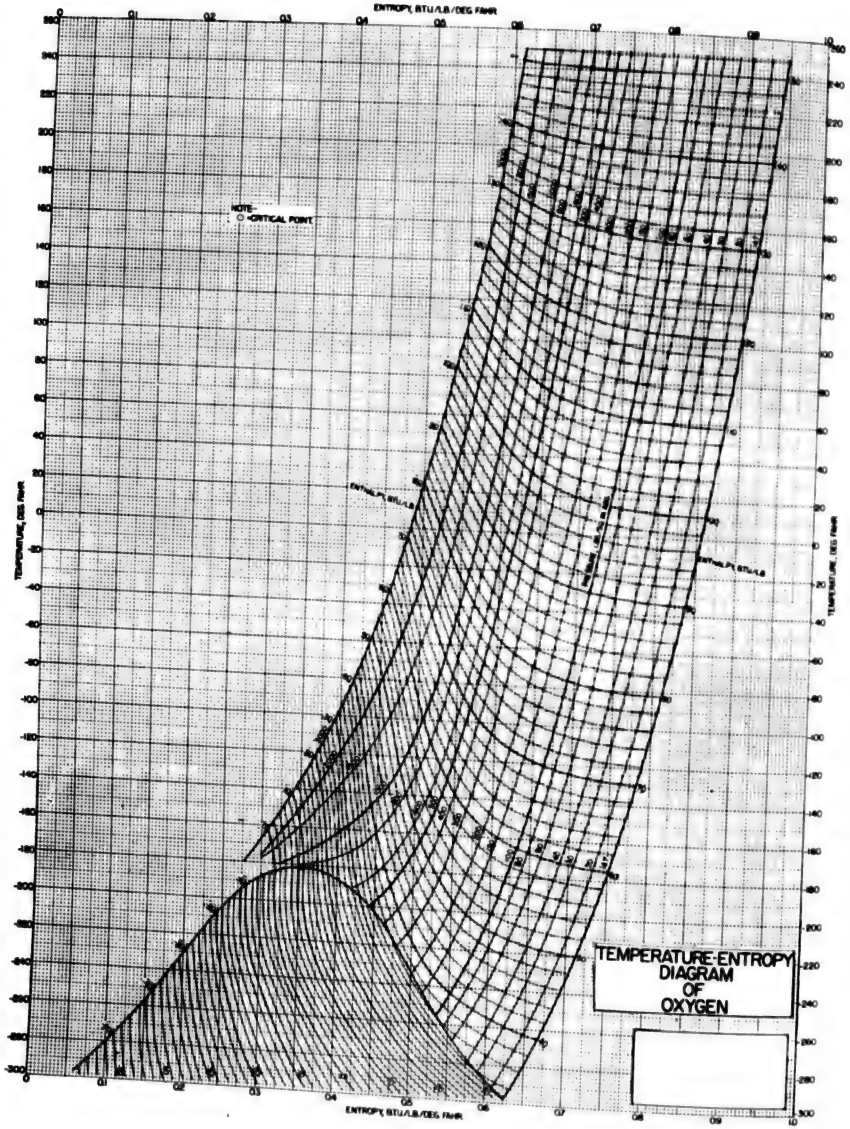
VAPOR PRESSURE
OF
OXYGEN
PRESSURE, LBS/SQ IN ABS
TEMPERATURE, DEG FAHR

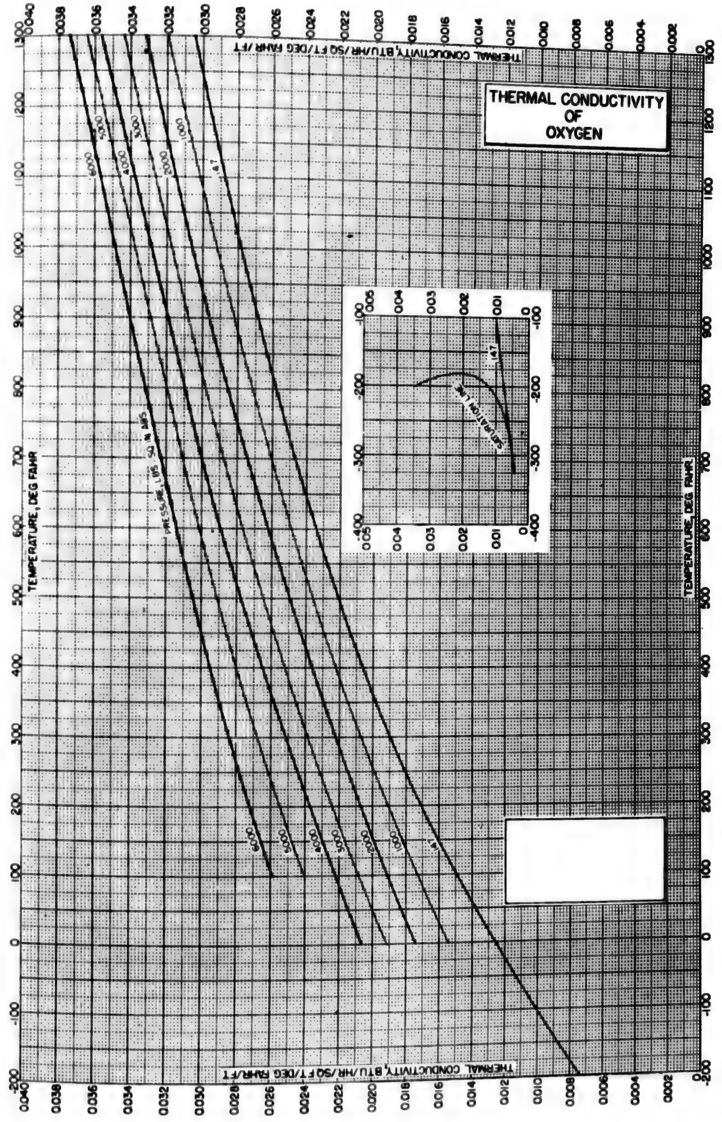


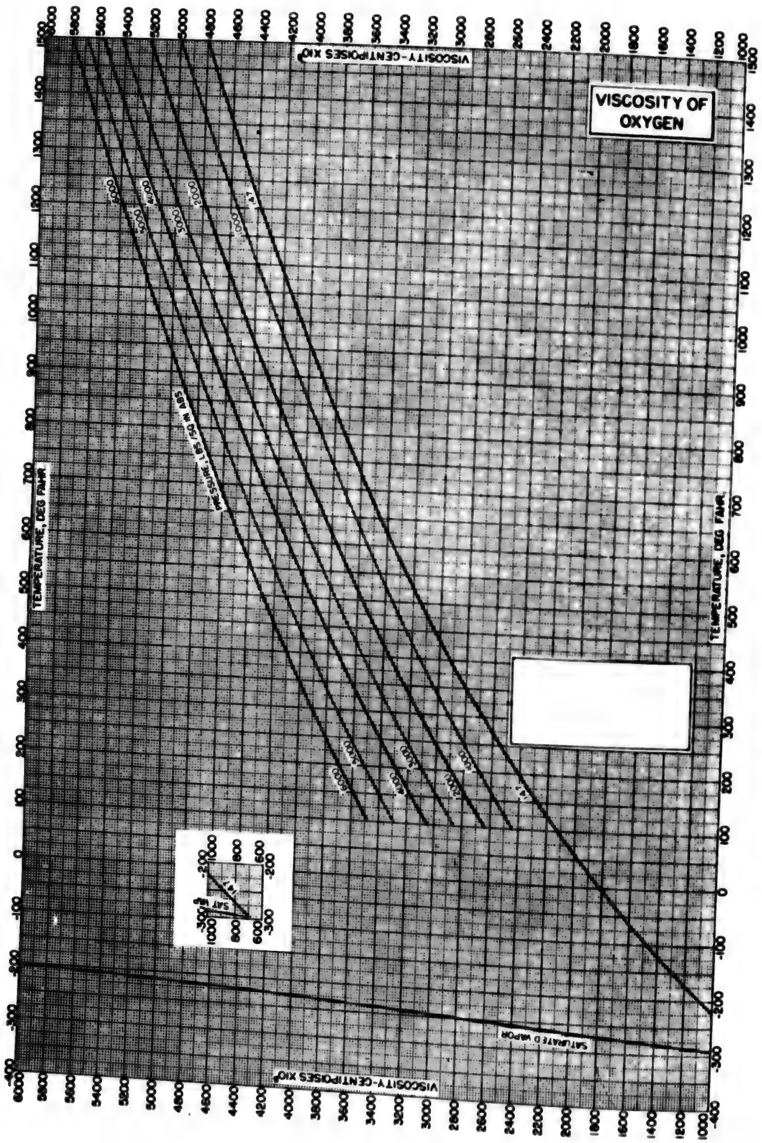
G-605.60



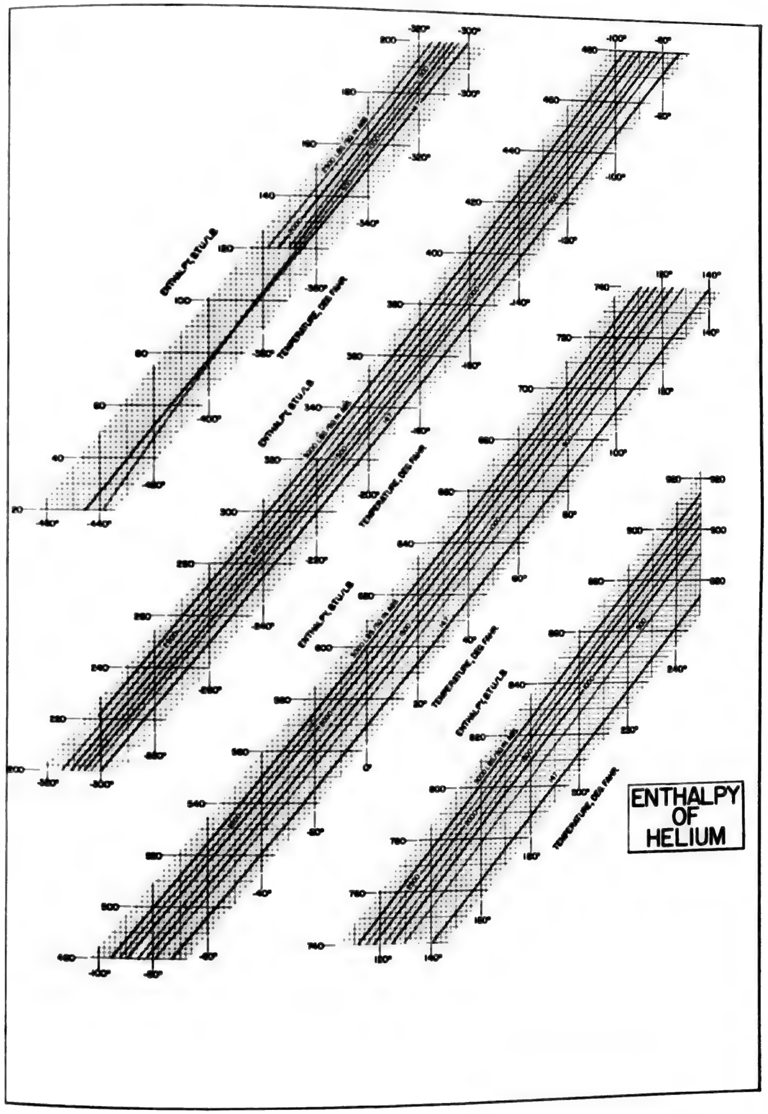
G-605.65


TEMPERATURE-ENTROPY
DIAGRAM
OF
OXYGEN
NOTE-
○ -CRITICAL POINT
ENTROPY, BTU/LB/DEG FAHR
TEMPERATURE, DEG FAHR

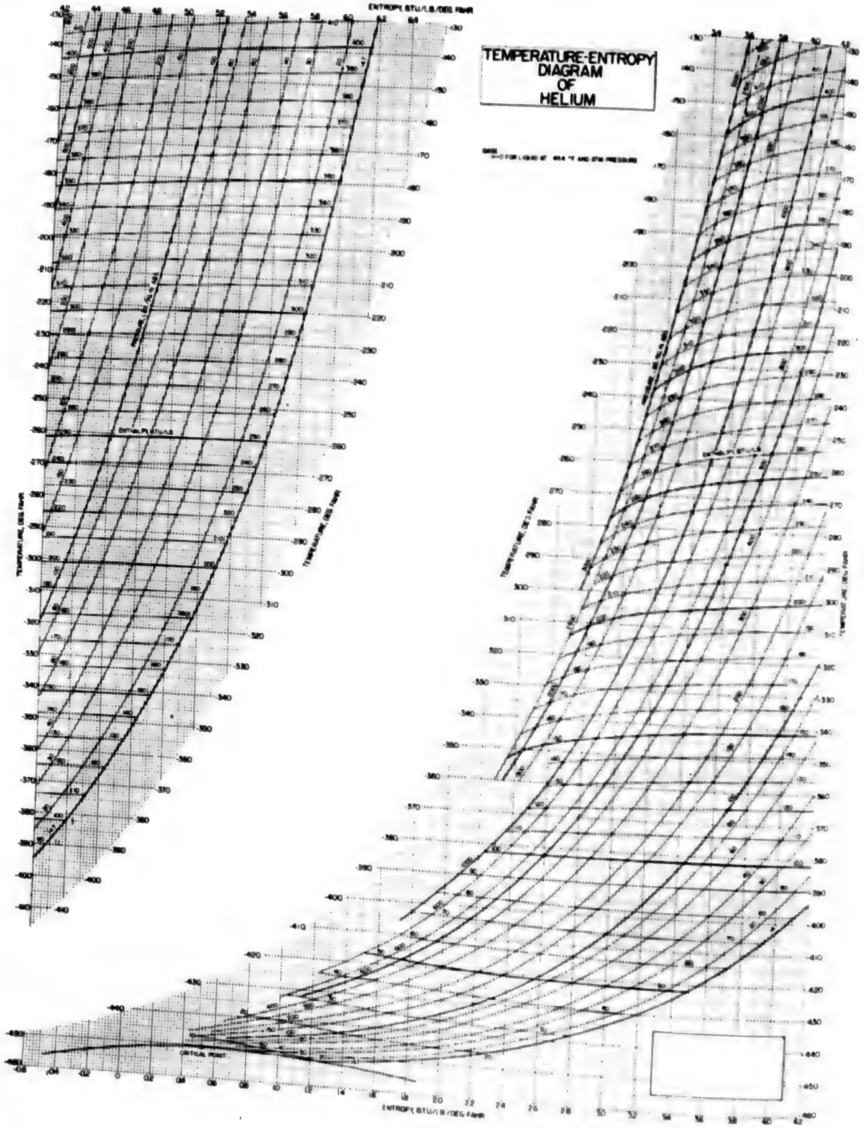

THERMAL CONDUCTIVITY
OF
OXYGEN
THERMAL CONDUCTIVITY, BTU/HR/SQ FT/DEG FAHR/FT
TEMPERATURE, DEG FAHR
PRESSURE, LBS. SQ IN ABS
14.7
1000
2000
3000
4000
5000
6000
SATURATION LINE

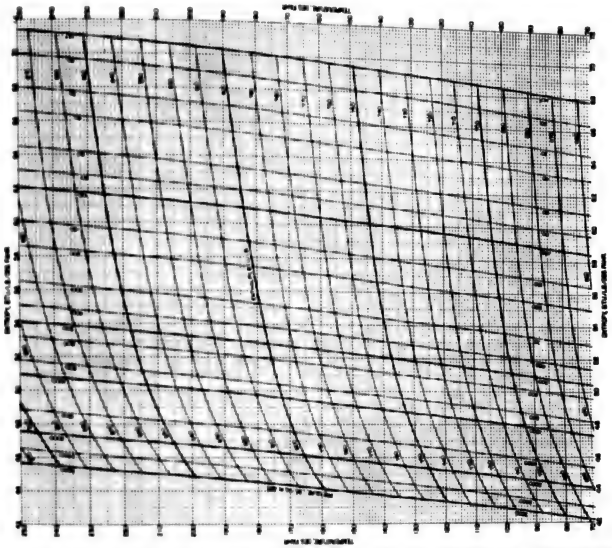


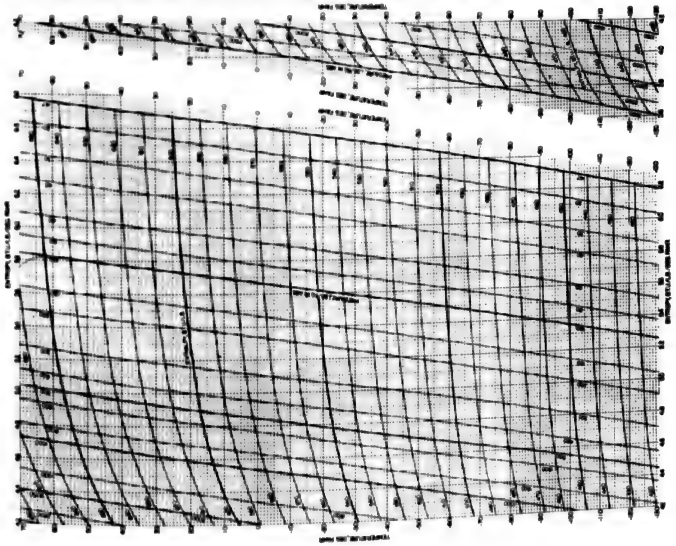
G-605.90

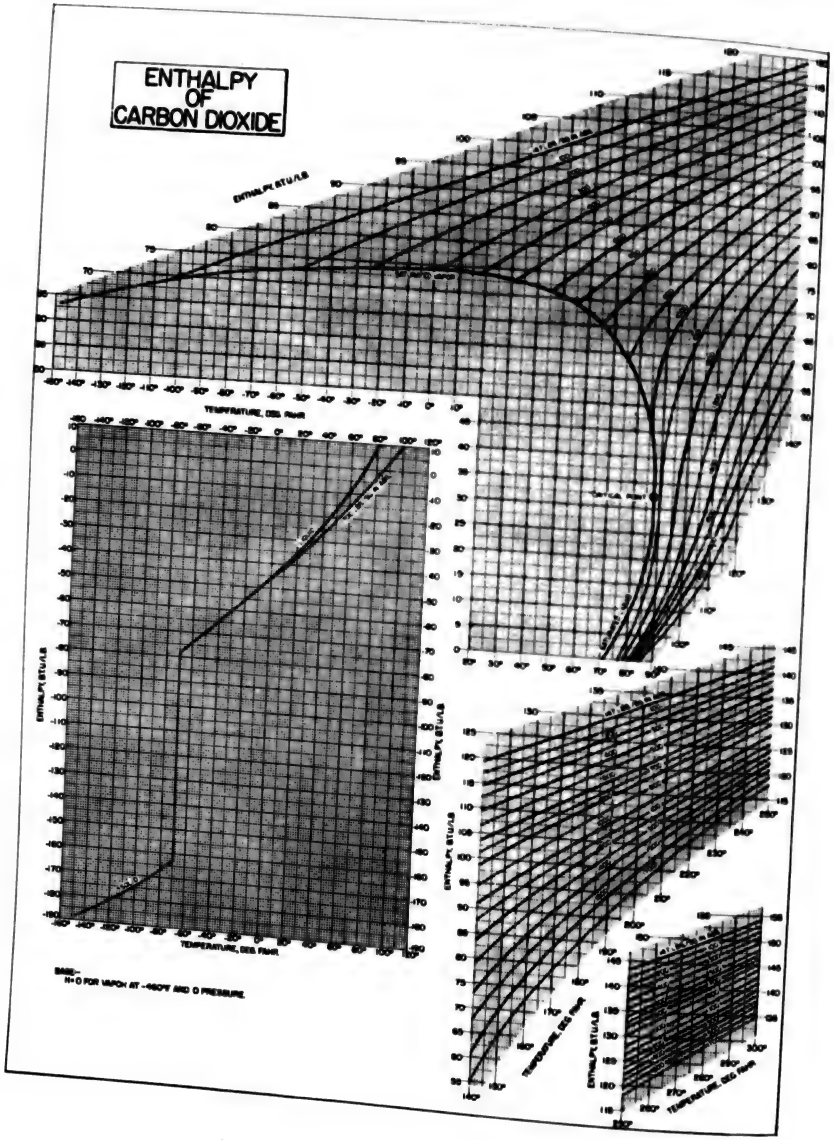


G-609.30

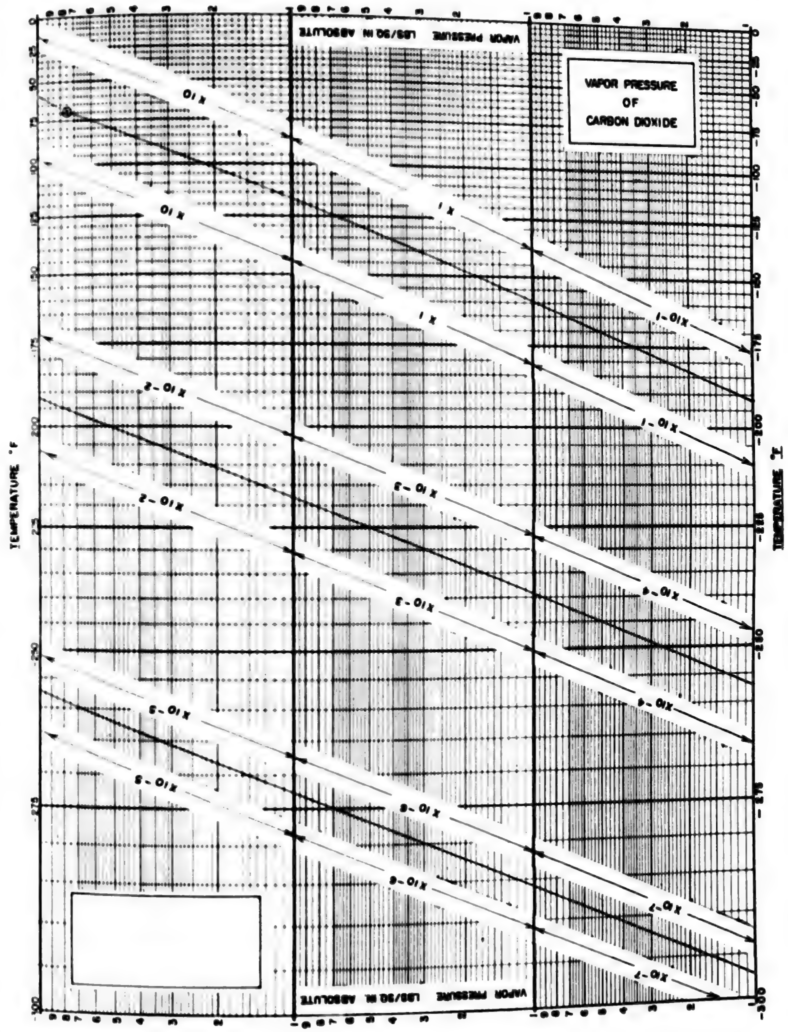

TEMPERATURE-ENTROPY
DIAGRAM
OF
HELIUM
ENTROPY, BTU/LB/DEG FAHR
TEMPERATURE, DEG FAHR
CRITICAL POINT





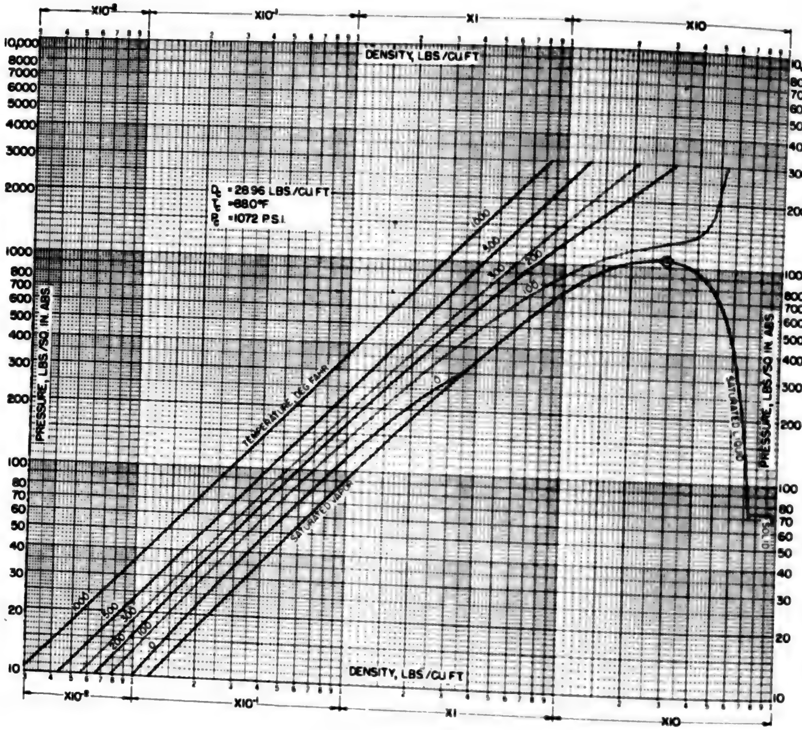


G-675.30

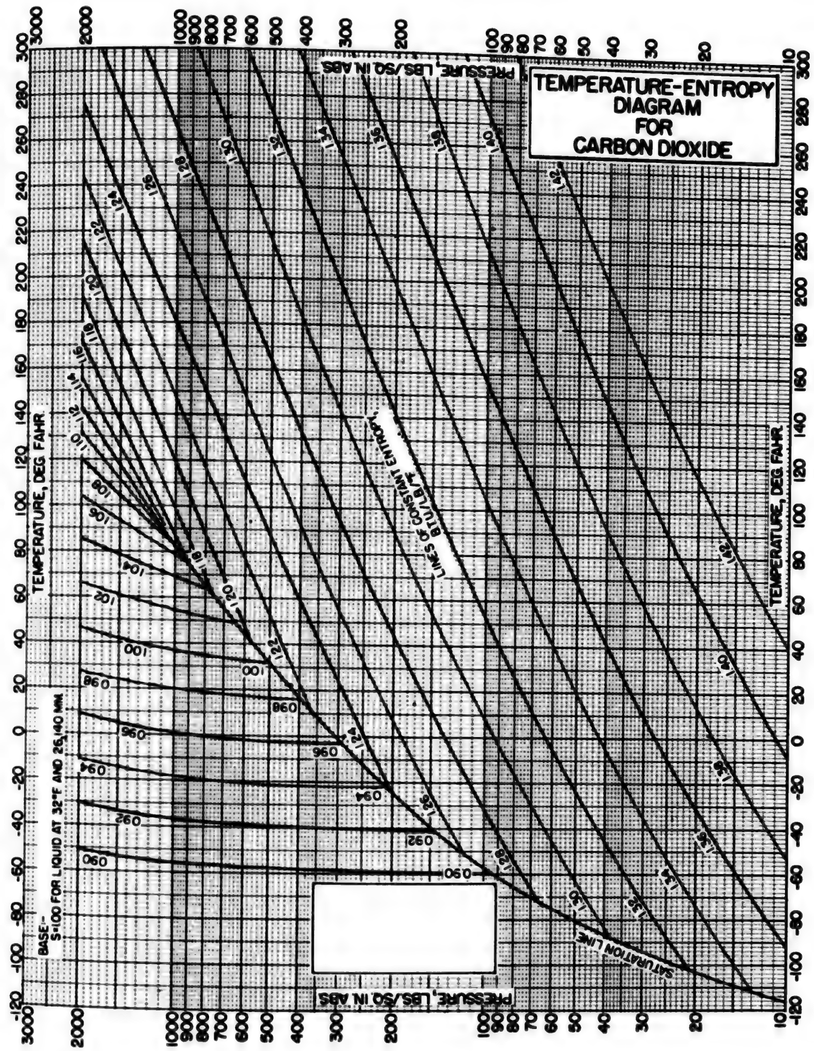


G-675.51

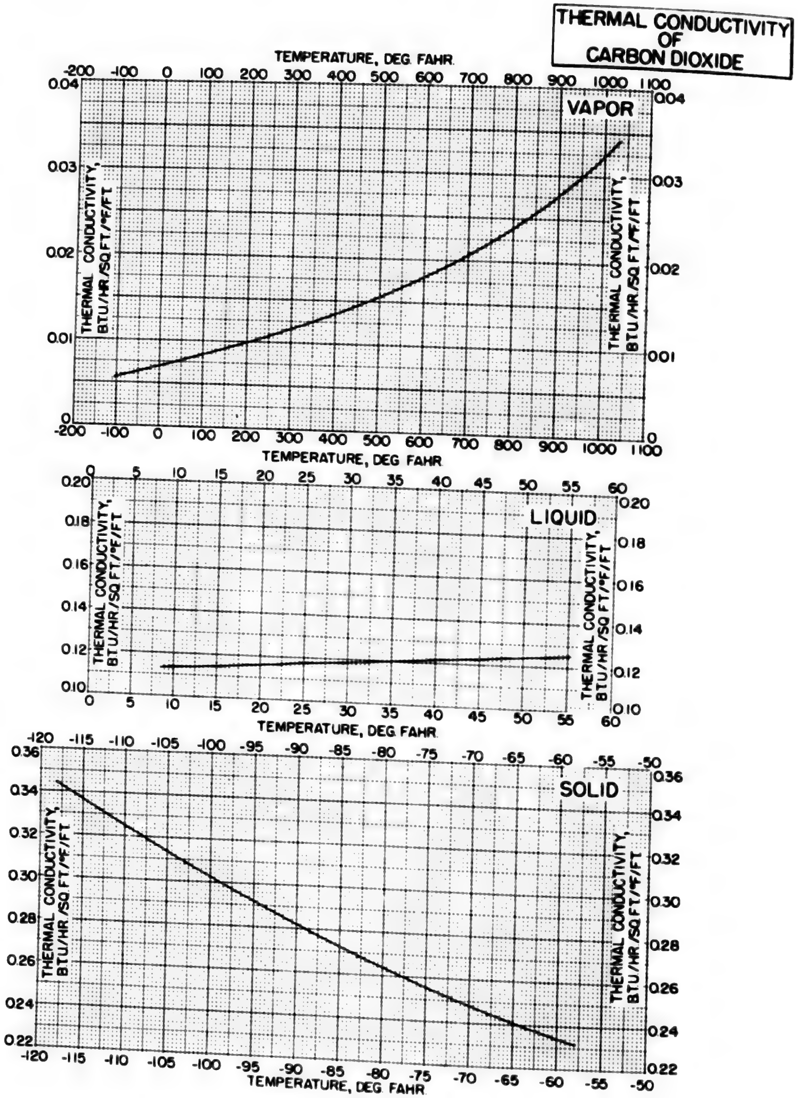
DENSITY OF CARBON DIOXIDE



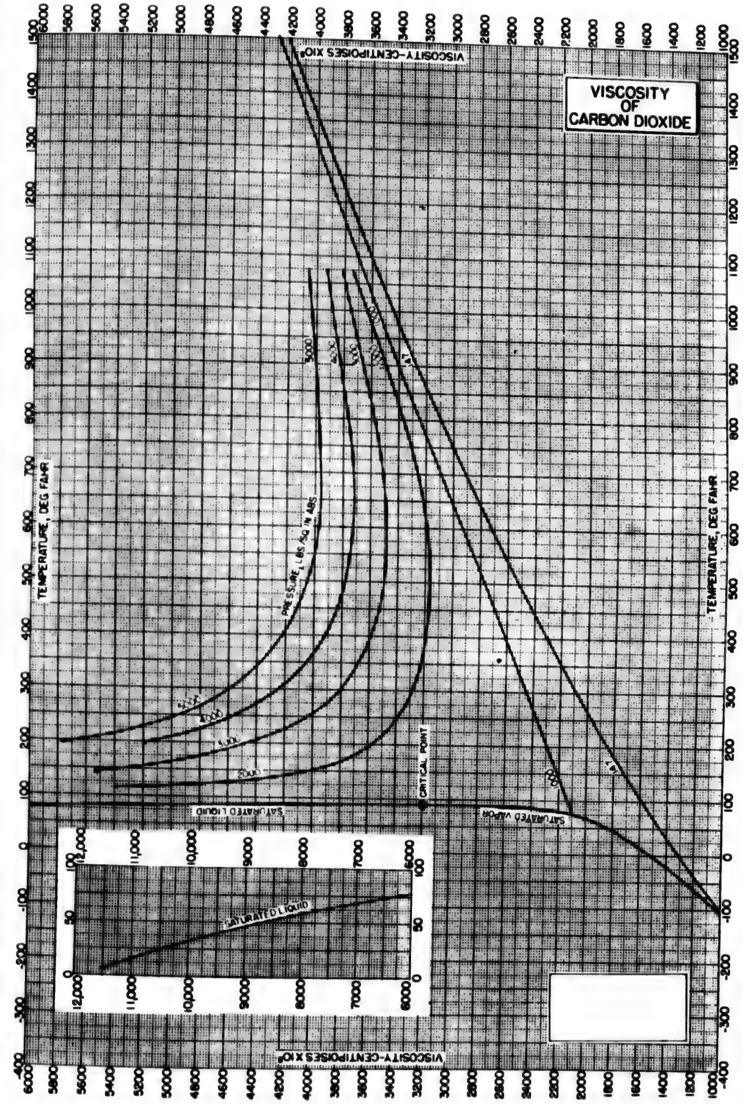
G-675.60



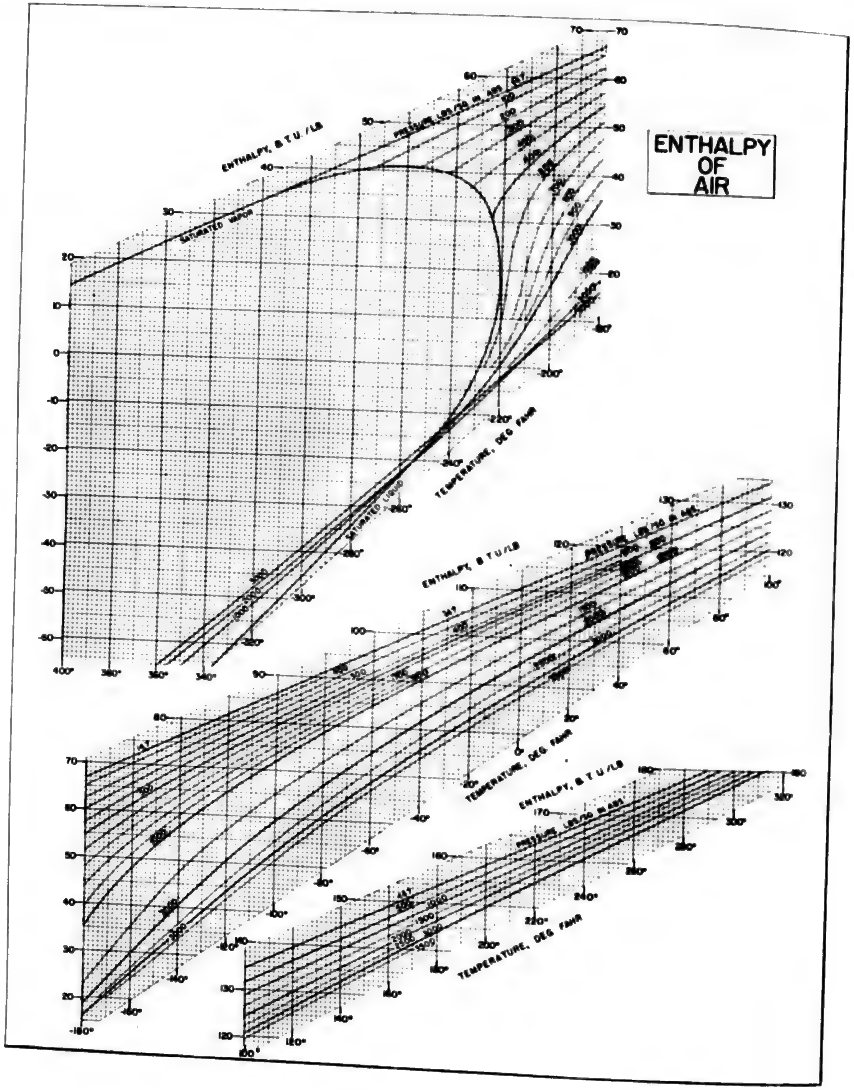
G-675.65



G-675.80



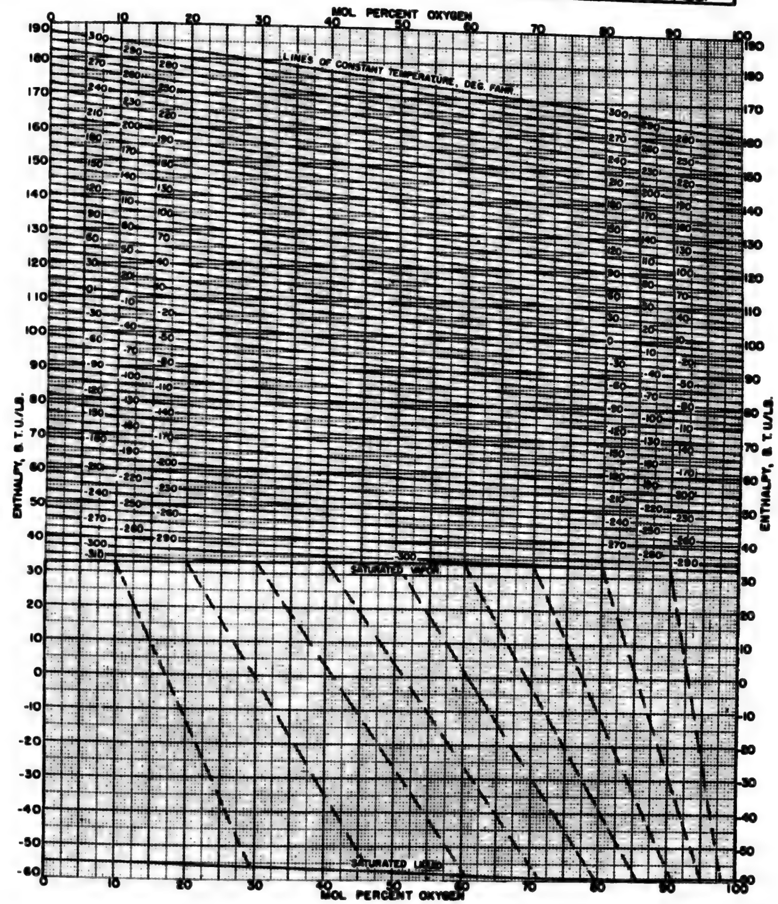
G-675.90



G-815.30

BASE:—
OXYGEN— H=O FOR VAPOR AT -460°F AND O PRESSURE.
NITROGEN—H=O FOR VAPOR AT -460°F AND O PRESSURE.

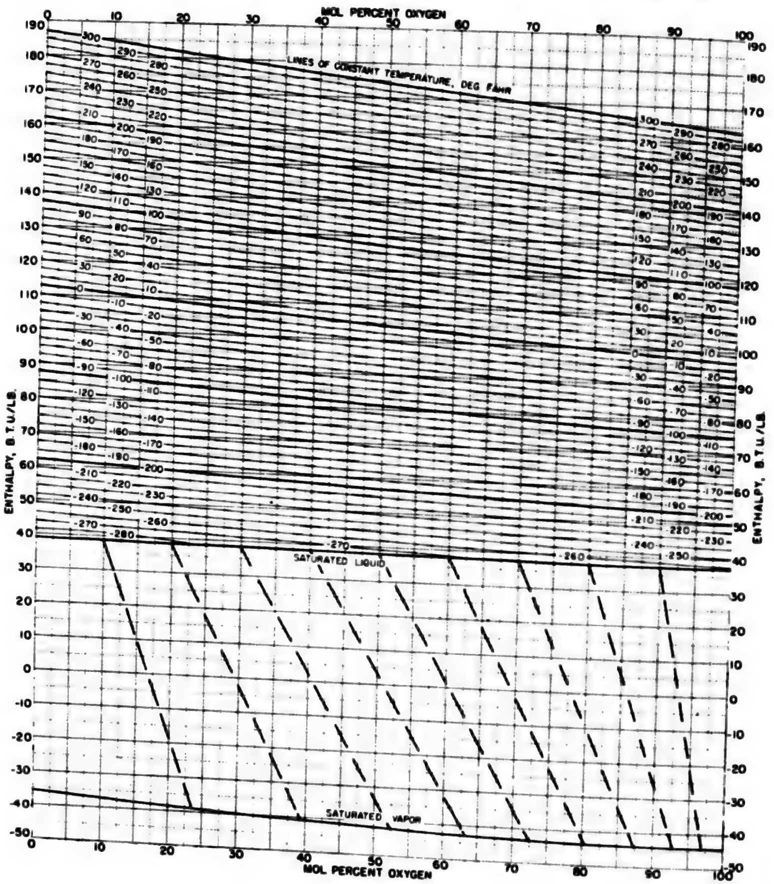
ENTHALPY
OF
OXYGEN-NITROGEN MIXTURES
AT 14.7 LBS/SQ.IN.ABS.



G-815.31

BASE:-
OXYGEN - H=O FOR VAPOR AT -460°F AND O PRESSURE.
NITROGEN - H=O FOR VAPOR AT -460°F AND O PRESSURE.

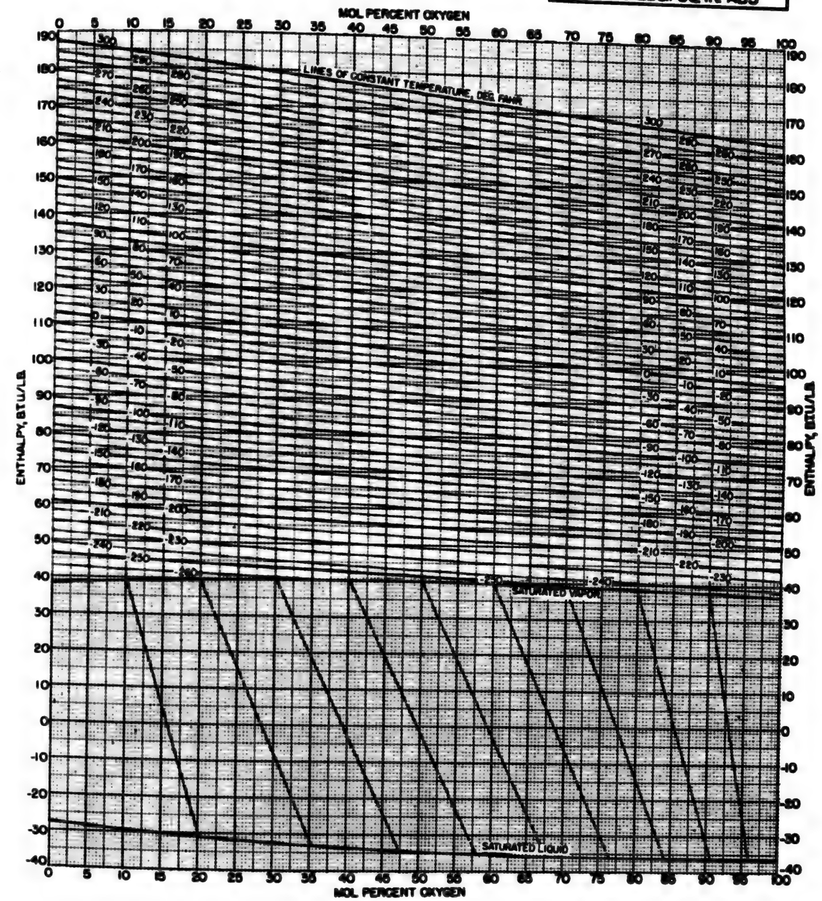
ENTHALPY OF OXYGEN-NITROGEN MIXTURES AT 75 LBS./SQ. IN. ABS.



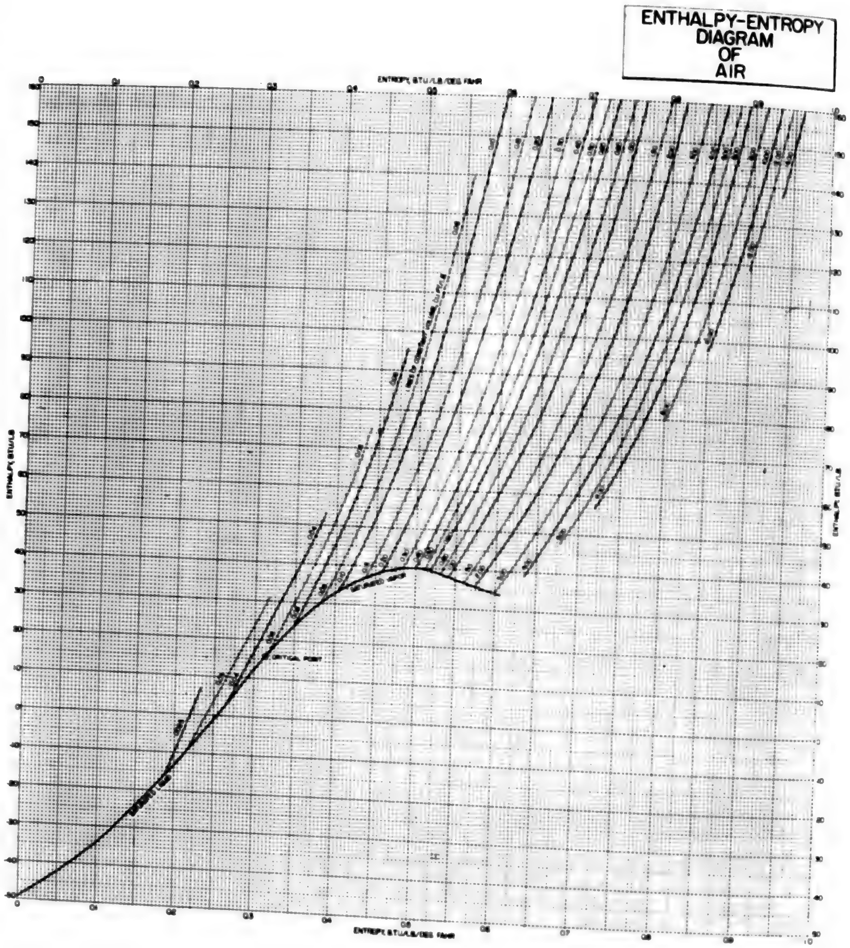
G-815.32

BASE:-
H=O FOR VAPOR AT -460°F AND O PRESSURE.

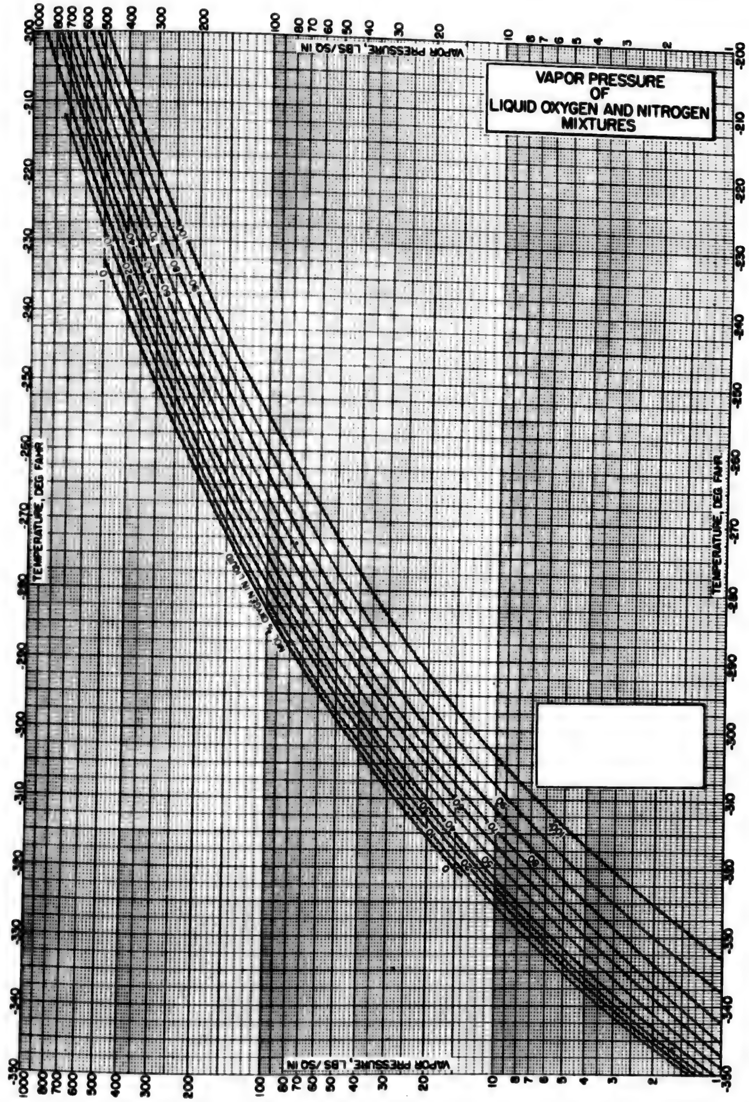
ENTHALPY OF OXYGEN-NITROGEN MIXTURES AT 150 LBS./SQ. IN. ABS



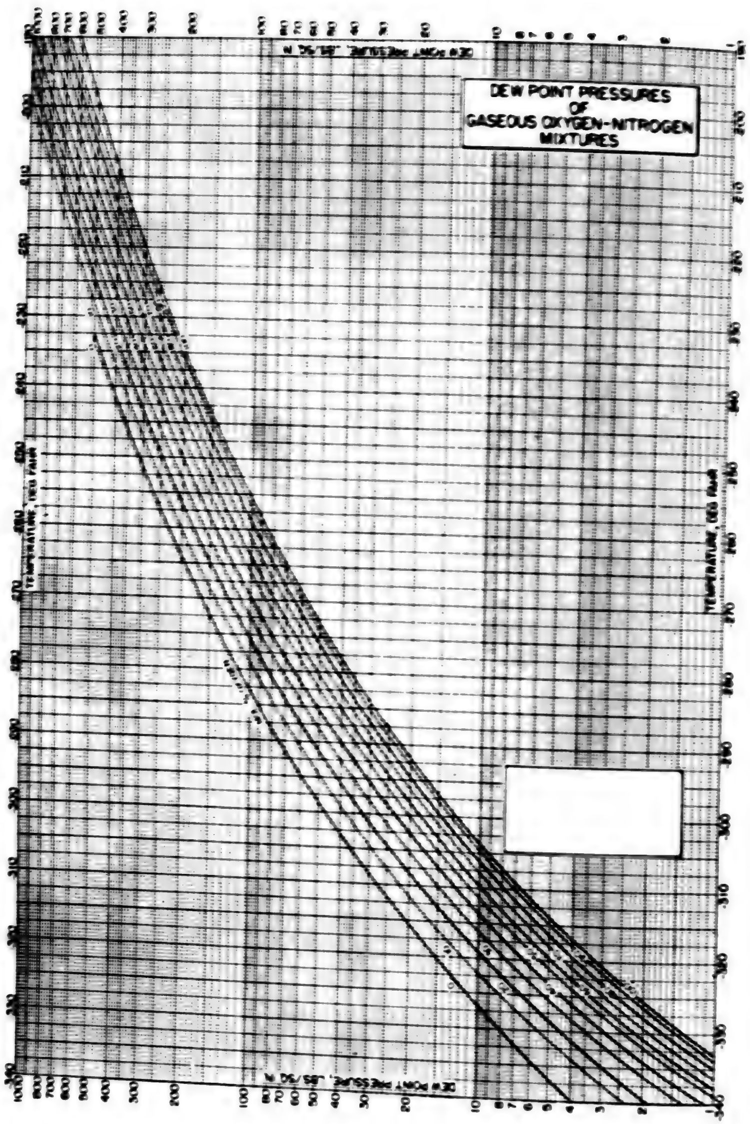
G-815.33



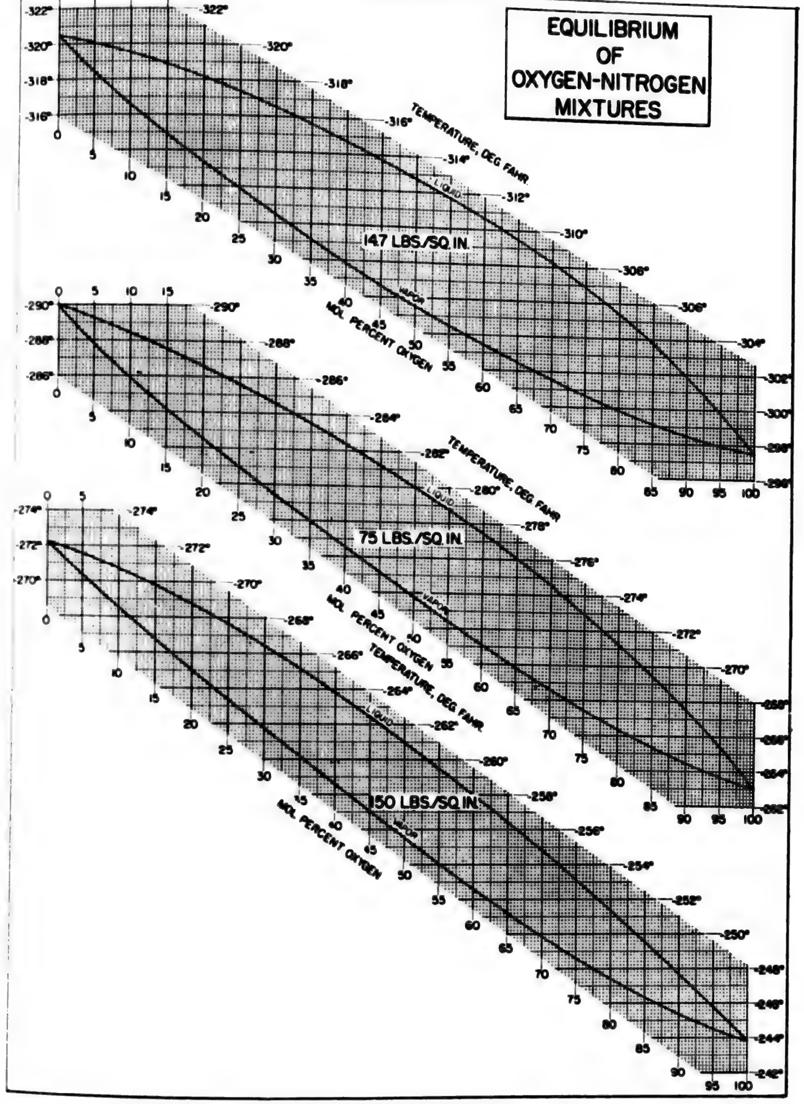
G-815.34



G-815.50

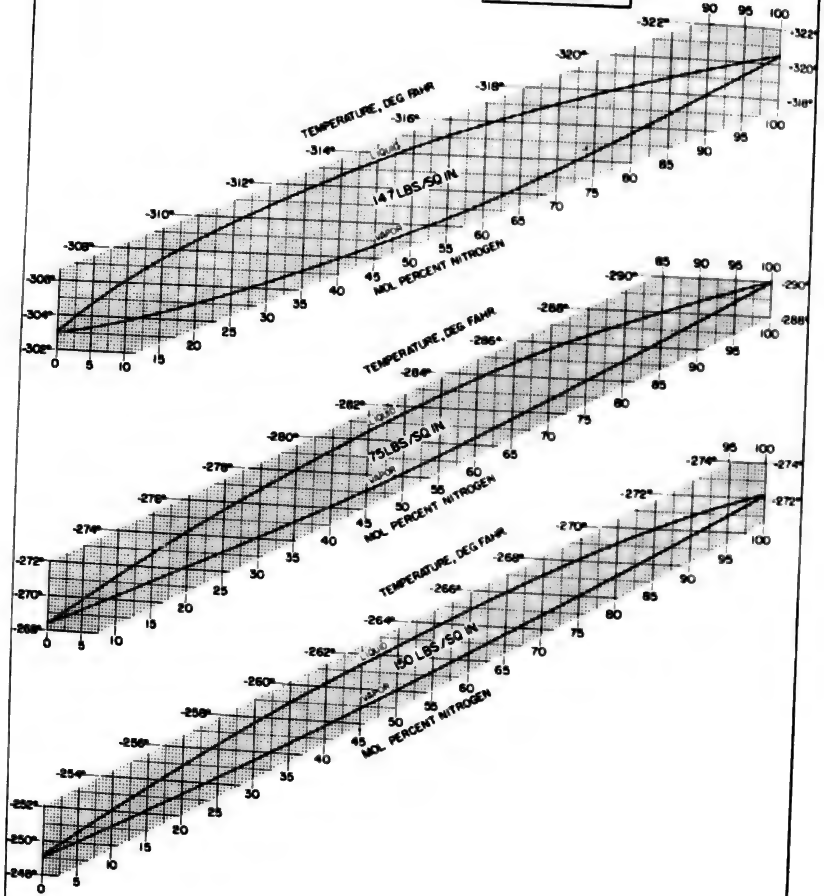


G-815.51



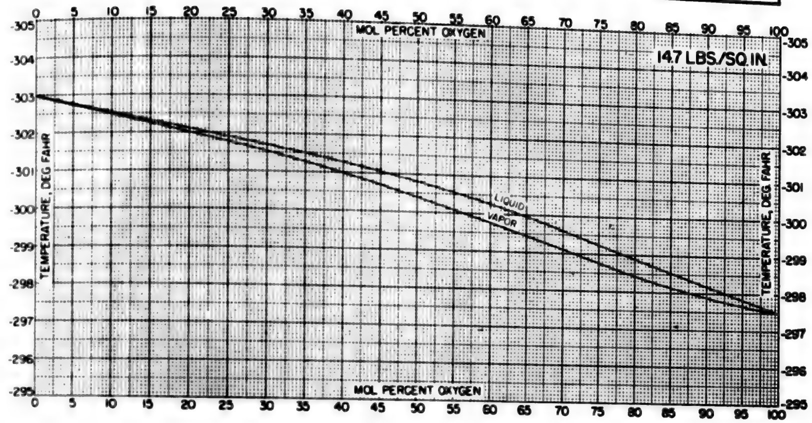
G-815.52

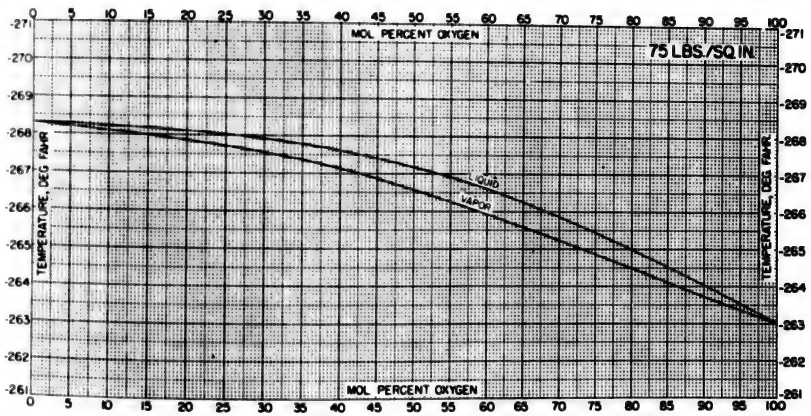
EQUILIBRIUM OF NITROGEN-ARGON MIXTURES



G-815.53

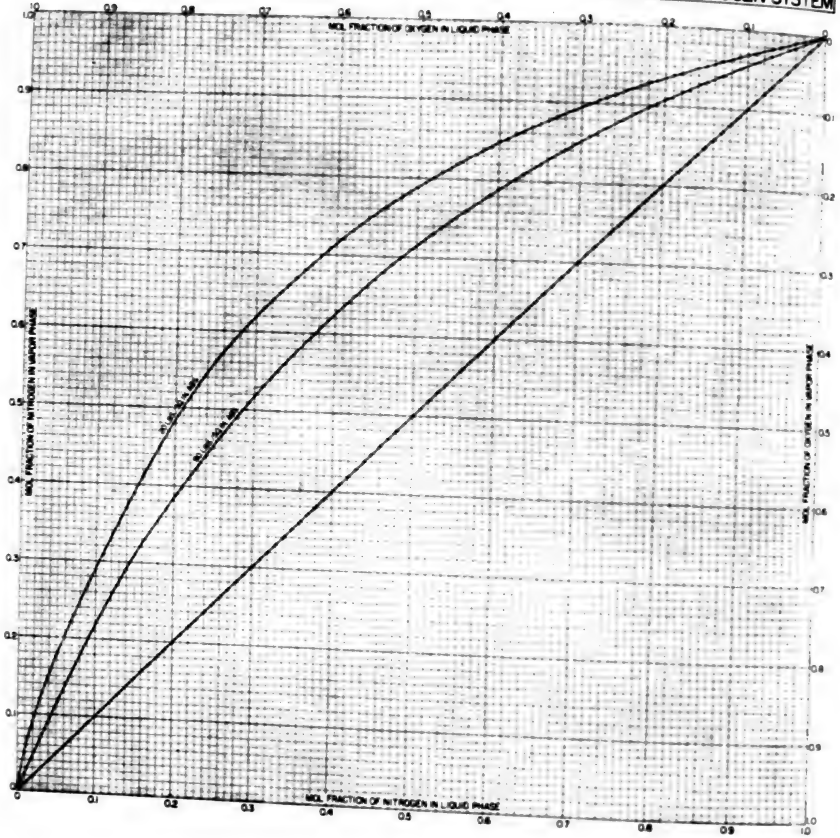
EQUILIBRIUM OF OXYGEN-ARGON MIXTURES





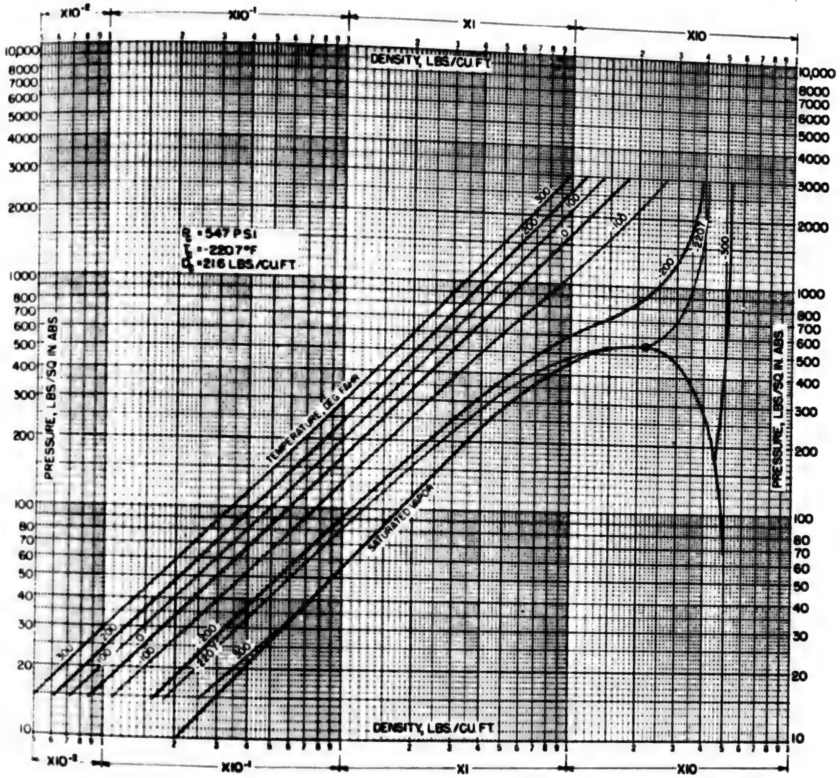
G-815.54

LIQUID-VAPOR EQUILIBRIUM FOR OXYGEN-NITROGEN SYSTEM

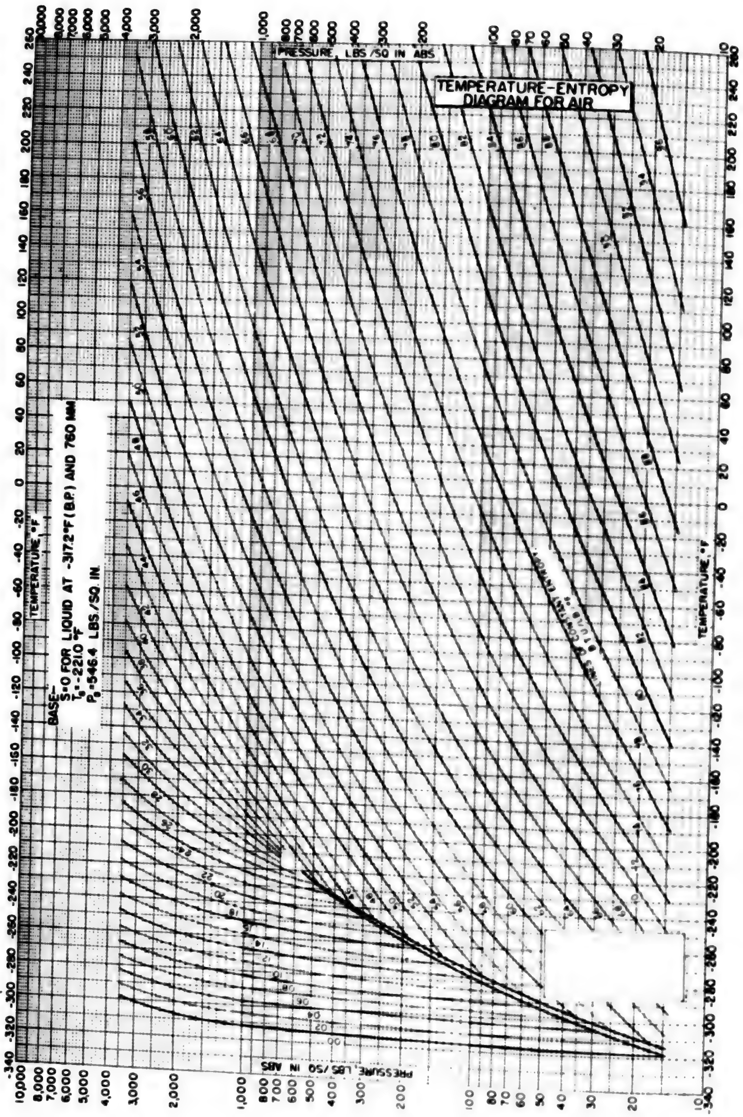


G-815.56

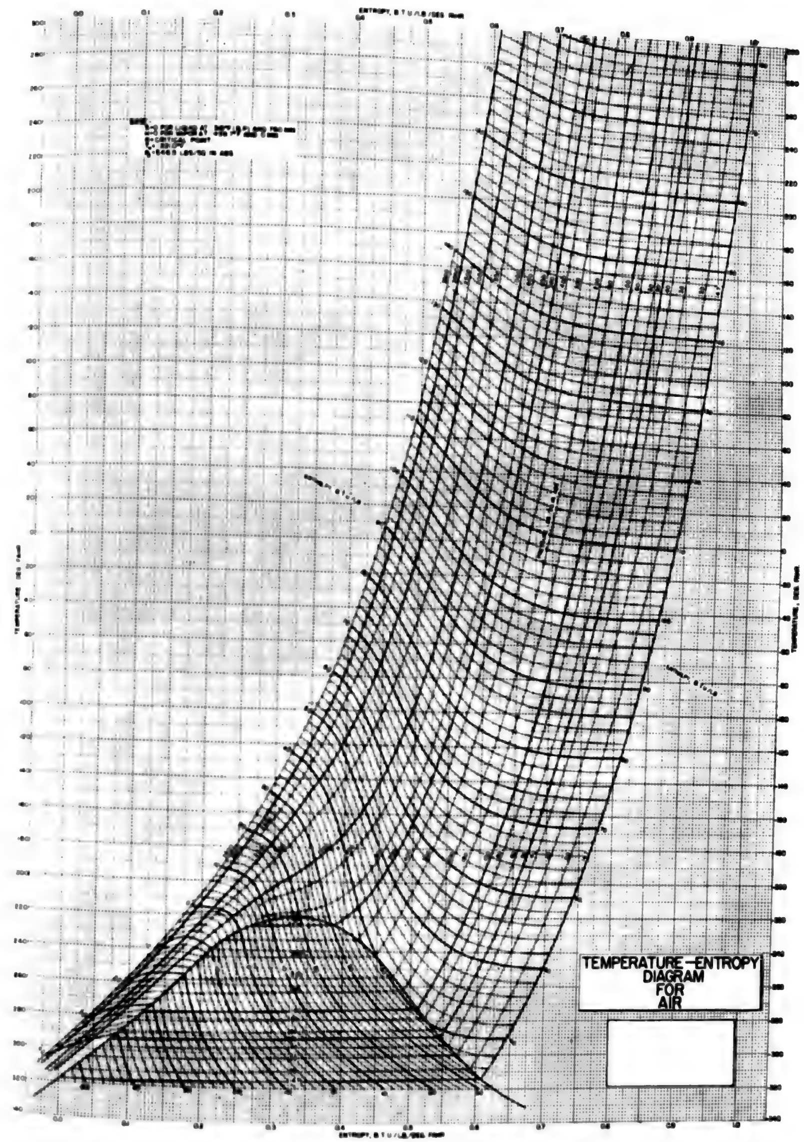
DENSITY OF AIR



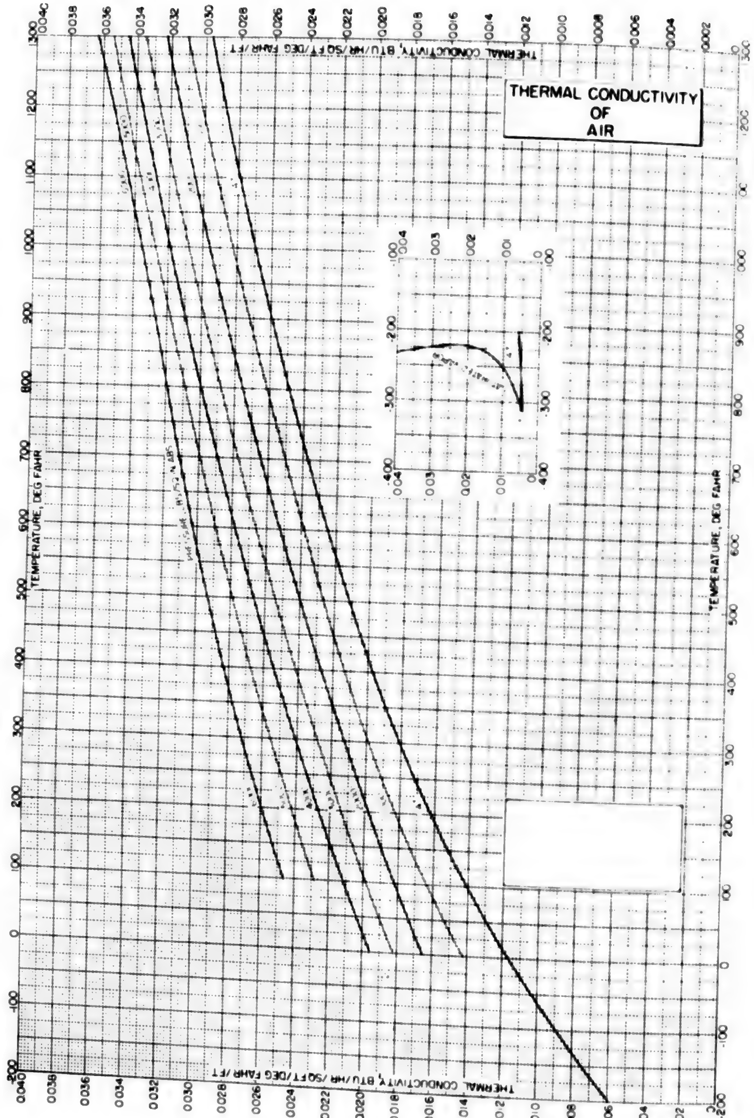
G-815.60

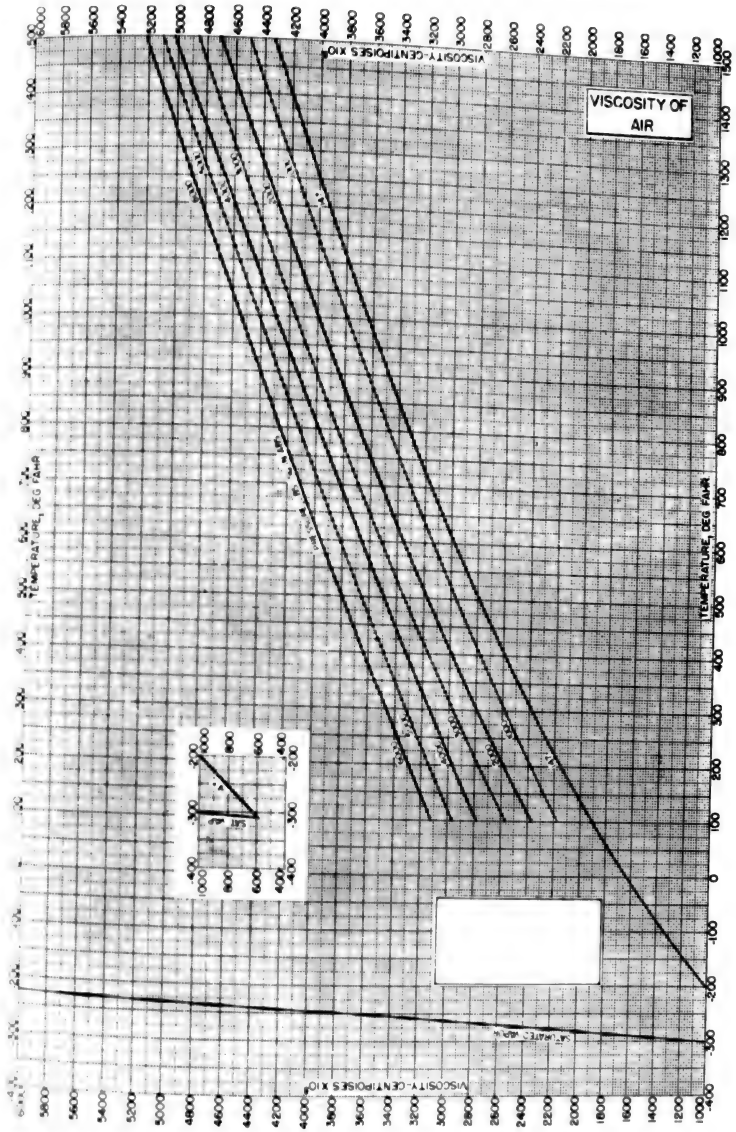


G-815.65

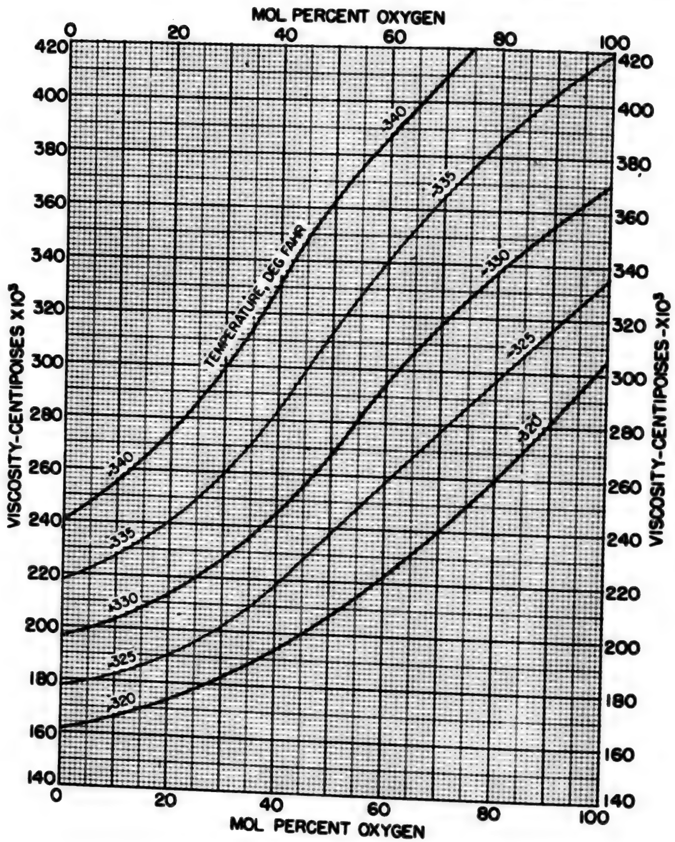


G-815.66


THERMAL CONDUCTIVITY
OF
AIR
THERMAL CONDUCTIVITY, BTU/HR/SQ FT/DEG FAHR/FT
TEMPERATURE, DEG FAHR


VISCOSITY OF
AIR
VISCOSITY-CENTIPOISES X10
TEMPERATURE, DEG FAHR

VISCOSITY OF LIQUID NITROGEN-OXYGEN MIXTURES



G-815.91

GLOSSARY

AMBIENT.	Surrounding atmosphere.
API.	Armor-piercing, incendiary (bullets).
ATPD.	Air temperature—pressure deviation.
BHP.	Brake horsepower.
BOTTOMS.	That part of the liquid which is drawn off from the lower part of the tower.
BTPS.	Body temperature pressure saturated. Temperature and pressure under saturated conditions in the body.
BTU.	British thermal unit.
CE.	Exit concentration.
CGSU.	Centimeter gram second units.
CFH.	Cubic feet per hour.
CFM.	Cubic feet per minute.
CHELATE COMPOUND.	An organic compound in which atoms of the same molecule are coordinated.
CL.	Center line.
CO.	Entering concentration.
COLD BOX.	That portion of a mechanical oxygen plant containing the fractionation column and low-temperature heat exchanger equipment.
CO-SAL-EN.	Cobalt salicylaldehyde ethylenediamine.
CO-X-SAL-EN.	X-substituted salicylaldehyde ethylenediamine cobalt.
CP.	Specific heat of a gas.
CV-1, etc.	Refer to control valve No. 1 etc., on flow sheets.
C4B, etc.	Refer to unit parts of the flow sheet.
EN.	Ethylenediamine.
ETHACOL.	O-ethoxyphenol.
ETHOMINE.	Cobalt 3-ethoxy salicylaldehyde ethylenediamine.
ETMMGBR.	Ethyl magnesium bromide.
FLUOMINE.	Cobalt 3-fluro salicylaldehyde ethylenediamine.
FPM.	Feet per minute.
FROST (DEW) POINT.	The boundary temperature at which ice (water) is deposited upon a surface.
HETP.	Height of a packed column equivalent to a theoretical plate.
HP.	Horsepower.
HTU.	Height of a transfer unit.
ID.	Inside diameter.
JOULE-THOMPSON.	The change in enthalpy produced by the direct expansion of a gas.
KCAL/MOLE.	Kilogram-calorie per mole.
L/MIN.	Liters per minute.
LP-1.	Low-pressure Model 1.
LPAS-3.	Low-pressure air transportable Model 3.
LPS-2.	Low-pressure skid model.
MEMMGI.	Methyl magnesium iodide.
METHOMINE.	Cobalt 3-methoxy salicylaldehyde ethylenediamine.
MG/L.	Milligrams per liter.
MSA.	Mine Safety Appliance Company (Hopcalite).
M-2, M-F, etc.	Designation of plants described in Chapters 3 and 4.
M-F.	Designation of a low-pressure mechanical method for separation of oxygen from air (Chapter 2).
NBS.	National Bureau of Standards.
OD.	Outside diameter.
O-ETHOVAN.	3-ethoxysalicylaldehyde.
OVERHEAD.	That part of the gas which is drawn off from the top of the tower.
PAULING METER.	Instrument for determining the magnetic susceptibility of a mixture of gases.
PRTN.	Bis-trimethylenetriamine.
PRODUCTIVITY (P).	Actual amount of oxygen produced under cycling conditions.
PSI.	Pounds per square inch gauge pressure.
PSIA	Pounds per square inch absolute pressure.
REVERSING EXCHANGERS.	Multiple pass heat exchanger in which counter current gas streams are switched at intervals so that a reversal of flow results in a given pass from period to period.
RPM.	Revolutions per minute.
SALCOMINE.	Salicylaldehyde ethylenediamine cobalt (active form).
SATURATION (S).	A measure of the amount of the compound present which is capable of absorbing oxygen.

SCF.	Standard cubic feet—volume at 60 F and 1 atmosphere pressure.
SCHIFF'S BASE.	Condensation product of an aliphatic amine and an aromatic aldehyde.
S.L.	Sea level.
STEDMAN-COLUMN.	A particular type of fractionation column packing (Chapter 5).
STP.	Standard temperature and pressure.
SWITCH EXCHANGERS.	Heat exchangers which are switched from one gas stream to another.
SYLPHON CONTROL.	A pressure control device with a metal "sylphon" bellows.
TFE.	Tetrafluoroethane.
TURBULATOR STRIP.	A twisted strip inserted in tubing to produce turbulent flow.

BIBLIOGRAPHY

Numbers such as Div. 11-101-M1 indicate that the document listed [illegible] microfilm index printed in a separate volume. For access to the [illegible] that its title appears Army or Navy agency listed on the reverse of the half-title page. [illegible] the microfilm, consult

Chapter 2

1. [illegible] Report of NDRC Oxygen Reviewing Committee, [illegible] Dalton, Harry A. Curtis, and others, Dec. 22, 1941. Div. 11-101-M1
2. [illegible] Portable Plants for the Production of Liquid [illegible], Barnett F. Dodge, NDCrc-80, Yale University, [illegible] 1941. Div. 11-103.1-M2
3. [illegible] Production of Liquid Oxygen, Barnett F. Dodge and Harding Bliss, NDCrc-80, Yale University, Aug. 1, 1941. Div. 11-103.1-M3
4. Processes for the Manufacture of Liquid Oxygen from Air, Harding Bliss, Yale University, Jan. 15, 1942. Div. 11-103.1-M4
5. [illegible] Oxygen Program of Section 11.3, including Bi-Monthly Report for December 1942 and January 1943 prepared for a meeting with NDRC Reviewing Committee, Feb. 13, 1943. Div. 11-102-M3
6. Résumé of Oxygen Program, Section 11.1, Jan. 12, 1944.
7. Information and Diagram of Several Air Separation Cycles, Frederick G. Keyes, NDCrc-182, Special Report 5, MIT, May 16, 1942. Div. 11-103.4-M1
8. Analysis of Low Temperature Air Separation and Gas Liquefaction Cycles, Report to January 1, 1943, Barnett F. Dodge and Harding Bliss, OSRD 1424, OEMsr-232, Project NLB-6, Yale University, May 17, 1943. Div. 11-103.4-M4

SUPPLEMENTARY

9. Portable Oxygen Generating Plant from Navy BuS to [illegible], NRL, Oct. 31, 1942.
10. Large Oxygen Producing Units, Wolcott Dennis, NDCrc-206, Air Reduction Company, Inc., December 1943. Div. 11-102.1-M5
11. Conference on Small Oxygen Units, C. C. Furnas, The M. W. Kellogg Company, July 13, 1942. Div. 11-102.11-M1
12. Comparison of M-2 and MIT Oxygen Producing Units, George T. Skaperdas, M. W. Kellogg Company, Oct. 5, 1942.
13. [illegible] Liquid Air Rectification Cycles, Roger Adams and Harris M. Chadwell, OSRD 780, OEMsr-454, [illegible] NLB-42, Aug. 10, 1942. Div. 11-103.4-M2
14. The Development of a Low Temperature Engine-Compressor-Rectifier Unit for the Separation of Oxygen from Air, Frederick G. Keyes and S. C. Collins, Sept. 12, 1941. Div. 11-102.1-M1
15. [illegible] Oxygen Unit, Frederick G. Keyes, NDCrc-182, MIT, [illegible] 27, 1942. Div. 11-102.111-M1
16. Oxygen Producer, Designed and Built by S. C. Collins at Research Laboratory of Physical Chemistry, Frederick G. Keyes, NDCrc-182, Special Report 12, MIT, Sept. [illegible] 1942. Div. 11-102.111-M2
17. Instructions for Operating the Mond-Ricardo British Oxygen Gas Producer, Appendix of Memoranda Pertaining to Its Construction, Servicing, and Maintenance, Frederick G. Keyes, MIT, Sept. 28, 1942. Div. 11-102.111-M3
18. A Brief Comparison of Low Temperature Cycles for Producing Liquid Oxygen from Air, Barnett F. Dodge, Yale University, Feb. 15, 1942. Div. 11-103.1-M5
19. Tentative Outline of Program of Experimental Investigations for NDRC & Present Status of This Work, Barnett F. Dodge, Mar. 18, 1942.
20. High Pressure Liquid Oxygen Plant Originally Intended as Cascade System as Erected by Dr. W. F. Giauque, L. S. Twomey, NDCrc-198, University of California, Apr. 26, 1944. Div. 11-103.1-M6

Chapter 3

1. The Development of a Low Temperature Engine-Compressor-Rectifier Unit for the Separation of Oxygen from Air, Frederick G. Keyes and S. C. Collins, Sept. 12, 1941. Div. 11-102.1-M1
2. Heat Interchangers for Gases, Alternating Flow Scrubber-Heat Exchanger, S. C. Collins, NDCrc-182, Special Reports 2 and 3, MIT, Mar. 9, 1942. Div. 11-104.13-M1
3. Compressors, Expansion Engine, Interchangers, Rectifiers, Frederick G. Keyes, Apr. 15, 1942.
4. Oxygen Producer, Designed and Built by S. C. Collins at Research Laboratory of Physical Chemistry, Frederick G. Keyes, Special Report 12, NDCrc-182, MIT, Sept. 25, 1942. Div. 11-102.111-M2
5. A Light-Weight, Automatic, Mechanical Generator, S. C. Collins and Howard O. McMahon, OSRD 3800, NDCrc-182, Service Projects AC-12, NS-116, CE-29, MIT, June 19, 1944. Div. 11-102.111-M7
6. Various Oxygen Producing Units, Monthly Progress Report, Walter E. Lobo, M. W. Kellogg Company, Mar. 19, 1942. Div. 11-102.1-M2
7. Some Consideration on the Removal of Water and Carbon Dioxide in Reversing Exchangers, Sept. 3, 1943. Div. 11-104.13-M8
8. The History of the Development of Heat Exchangers for Low Pressure Mobile Oxygen Units, Walter E. Lobo, M. W. Kellogg Company, Oct. 4, 1943. Div. 11-104.13-M5
9. Low Pressure [illegible] Oxygen Units Developed [illegible], Clark Brothers Company, Inc. and M. W. Kellogg Company, Oct. 29, 1943.
10. [illegible], Walter E. Lobo, M. W. Kellogg Company, March 1942 to January 1944. Div. 11-102.2-M2

11. *Oxygen Plant Development,* Walter E. Lobo, OSRD 4555, OEMsr-365, Service Projects NA-11, NS-115 and others, M. W. Kellogg Company, Feb. 28, 1945. Div. 11-102-M4

13. *Mechanical Oxygen Generating Units and Related Equipment,* J. N. MacKendrick and A. Van Campen, OSRD 4792, OEMsr-370, Service Projects AC-12, NA-111 and others, Clark Brothers Company, Inc., May 15, 1945. Div. 11-102.1-M8

14. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for May 1944,* J. H. Rushton, Barnett F. Dodge, and W. L. McCabe, OSRD 3861, OEMsr-934, University of Pennsylvania, July 7, 1944. Div. 11-101-M7

15. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for June 1944,* J. H. Rushton, Barnett F. Dodge, and W. L. McCabe, OSRD 3972, OEMsr-934, University of Pennsylvania, Aug. 2, 1944. Div. 11-101-M7

16. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for July 1944,* J. H. Rushton, Barnett F. Dodge, and W. L. McCabe, OSRD 4142, OEMsr-934, University of Pennsylvania, Sept. 19, 1944. Div. 11-101-M7

17. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for September 1944,* J. H. Rushton, Barnett F. Dodge, and W. L. McCabe, OSRD 4302, OEMsr-934, University of Pennsylvania, Nov. 6, 1944. Div. 11-101-M7

18. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for January 1945,* J. H. Rushton, Barnett F. Dodge, and W. L. McCabe, OSRD 4732, OEMsr-934, University of Pennsylvania, Mar. 3, 1945. Div. 11-101-M7

19. *Methods of Production and Calibration of Combination Vapor Pressure and Gas Dial Thermometers,* Paul Erbguth and J. G. Aston, OSRD 4780, University of Pennsylvania, Jan. 26, 1945. Div. 11-104.2-M5

20. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for February 1945,* J. H. Rushton, Barnett F. Dodge, and W. L. McCabe, OSRD 4879, OEMsr-934, University of Pennsylvania, Mar. 30, 1945. Div. 11-101-M7

21. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for April 1945,* W. L. McCabe, OSRD 5153, OEMsr-934, University of Pennsylvania, May 31, 1945. Div. 11-101-M7

22. *Final Report of Central Engineering Laboratory, University of Pennsylvania, for the Period March 1943 through June 1945,* John A. Goff and Roy W. Banwell, OSRD 5482, OEMsr-934, Service Projects NLB-42, NA-106, and others, University of Pennsylvania, June 30, 1945. Div. 11-101-M9

23. *The Oxygen Program of Section 11.3, Including Bi-Monthly Report for December 1942 and January 1943 Prepared for a Meeting with NDRC Reviewing Committee,* Feb. 13, 1943. Div. 11-102-M3

24. *Oxygen Processes, Report to September 1, 1945,* O[illegible] 5928, NDCrc-206, Service Projects NS-115 and NS[illegible], Air Reduction Company, Inc., Oct. 1, 1945. Div. 11-103.[illegible]

SUPPLEMENTARY

25. *Airplane Oxygen Unit. Progress Report on the Possibility of Using the Phenomenon of Heat Transmission at Low Pressures as a Means of Detecting and Determining Gaseous Compositions,* data obtained by D. A. Williams, Aug. 8, 1942.

26. *Conference on Small Oxygen Units,* C. C. Furnas, M. W. Kellogg Company, July 13, 1942. Div. 11-102.11-M1

27. *Comparison of M-2 and MIT Oxygen Producing Units,* George T. Skaperdas, M. W. Kellogg Company, Oct. 5, 1942.

28. *Mobile Oxygen Units Liquid Air Fractionation Systems,* Walter E. Lobo, M. W. Kellogg Company, Feb. 3, 1943. Div. 11-103.4-M3

29. *Various Oxygen Producing Units, Monthly Progress Reports for Period from January 15 to February 15, 1943,* Walter E. Lobo, M. W. Kellogg Company. Div. 11-102.1-M2

30. *Various Oxygen Producing Units, Monthly Progress Report for Period from February 15 to March 15, 1943,* Walter E. Lobo, M. W. Kellogg Company, Mar. 23, 1943. Div. 11-102.1-M2

31. *Various Oxygen Producing Units, Monthly Progress Report for Period from March 15 to April 15, 1943,* Walter E. Lobo, M. W. Kellogg Company, Apr. 20, 1943. Div. 11-102.1-M2

32. *Various Oxygen Producing Units, Monthly Progress Report for Period from April 15 to May 31, 1943,* Walter E. Lobo, M. W. Kellogg Company, June 6, 1943. Div. 11-102.1-M2

33. *Various Oxygen Producing Units, Monthly Progress Report for Period from June 1 to July 1, 1943,* Walter E. Lobo, M. W. Kellogg Company. Div. 11-102.1-M2

34. *Various Oxygen Producing Units, Monthly Progress Report for Period from July 1 to July 27, 1943,* Walter E. Lobo, M. W. Kellogg Company. Div. 11-102.1-M2

35. Report dated November 1, 1943, summarizing the work on the M-2R unit at O'Fallon by J. Broadbent.

36. *Visit to Air Reduction Sales Company, December 15 and 16, 1943,* George T. Skaperdas, December 1943. Div. 11-102.1-M6

37. *Approximate Material Specifications for Clark M-7 Mobile Gaseous Oxygen Unit,* December 14, 1943.

38. *Process Calculations for 1000 SCFH Clark Mobile Gaseous Oxygen Unit M-7,* Walter E. Lobo, Dec. 15, 1943.

39. *Performance of M-7AT Radiators,* Eugene Miller, M. W. Kellogg Company, Apr. 16, 1945. Div. 11-102.141-M13

40. *Report Covering Consulting Services of Dr. Howard O. McMahon to E. B. Badger & Sons Company in Connection with Mechanical Oxygen Generators,* T. L. Wheeler and Howard O. McMahon, Arthur D. Little, Inc., M[illegible] 6, 1944. Div. 11-102.1-[illegible]

41. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for Period Beginning 1943 to January 31, 1944,* J. H. Rushton, Barnett F. Dodge, and others, University of Pennsylvania. Div. 11-101-M7

42. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for February 1944,* J. H. Rushton and Barnett F. Dodge, OSRD 3523, OEMsr-934, University of Pennsylvania, Apr. 25, 1944. Div. 11-101-M7

43. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for March 1944,* J. H. Rushton and Barnett F. Dodge, OSRD 3652, OEMsr-934, University of Pennsylvania, May 19, 1944. Div. 11-101-M7

44. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for April 1944,* J. H. Rushton and W. L. McCabe, OSRD 3760, OEMsr-934, University of Pennsylvania, June 9, 1944. Div. 11-101-M7

45. *The Collins Automatic Airborne Low-Pressure Oxygen Unit,* D. C. Reams, Jr., Central Engineering Laboratory, June 5, 1944. Div. 11-102.111-M6

46. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for August 1944,* J. H. Rushton, Barnett F. Dodge, and W. L. McCabe, OSRD 4207, OEMsr-934, University of Pennsylvania. Div. 11-101-M7

47. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for October 1944,* J. D. Rushton, Barnett F. Dodge, and W. L. McCabe, OSRD 4452, OEMsr-934, University of Pennsylvania. Div. 11-101-M7

48. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for November 1944,* J. R. Rushton, Barnett F. Dodge, and W. L. McCabe, OSRD 4516, OEMsr-934, University of Pennsylvania. Div. 11-101-M7

49. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for December 1944,* J. H. Rushton, Barnett F. Dodge, and W. L. McCabe, OSRD 4623, OEMsr-934, University of Pennsylvania. Div. 11-101-M7

50. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for March 1945,* W. L. McCabe, OSRD 5040, University of Pennsylvania. Div. 11-101-M7

51. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for April 1945,* W. L. McCabe, OSRD 5153, University of Pennsylvania. Div. 11-101-M7

52. *Progress Report November 15 to December 31, 1943, Semi-Portable Oxygen Unit M-6 Expander and Unit,* Wolcott Dennis.

53. *Report of All Work Done up to June 1, 1942, Toward the Development of: (a) Large Shipboard Oxygen Liquid Unit 4000 Lb/Hr; (b) Small Portable Gas Unit 300 Cu Ft/Hr,* Wolcott Dennis.

54. *Portable Oxygen Generating Plant Requirements* from Navy BuShips to Director, NRL, Oct. 31, 1942.

55. *Résumé of Oxygen Program,* Section 11.1, NDRC, Jan. 12, 1944.

56. *Mobile Oxygen-Nitrogen Generating Units,* #TM5-355, Technical Manual, U.S. War Department, Jan. 14, 1944. Div. 11-102.12-M7

57. *Minutes of Meeting on Field Generation of Oxygen Held in Pentagon Bldg., Washington, D.C., April 16, 1943,* from Maj. Gen. C. C. Williams.

58. *Oxygen Units under Development by the NDRC,* S. S. Prentiss, Jan. 1, 1943. Div. 11-101-M6

59. *The Oxygen Technical Committee, Morning Meeting,* Aug. 20, 1942. Div. 11-101-M4

60. *Oxygen Units under Development by the NDRC,* S. S. Prentiss, Aug. 14, 1942. Div. 11-101-M5

61. *Aircraft Mechanical Oxygen Generator,* Howard O. McMahon, June 15, 1944.

62. *Submarine Propulsion Committee, Minutes of First Meeting Held at Admiralty, December 1, 1936.*

63. *Closed Cycle Operating Characteristics of a Diesel Engine,* L. F. Campbell, W. E. Whybrew, and W. H. Sanders, NRL Report #0-2205, December 1943.

64. Some letters from S. C. Collins to E. P. Stevenson reporting on Collins' work.

Chapter 4

1. *Final Report of NDRC Oxygen Reviewing Committee,* T. R. Chilton, Harry A. Curtis, and others, Dec. 22, 1941. Div. 11-101-M1

2. *Oxygen Producing Units: (1) for Liquefied Oxygen Adapted for the Application of Precooling by Standard Freon 12 Refrigerating Machines; and (2) Shipboard Unit with Rectifier Having Rotating Packing,* Frederick G. Keyes, Dec. 17, 1943.

3. *Oxygen Generating Equipment, Report to June 30, 1945,* Frederick G. Keyes, OSRD 5329, NDCrc-182, NA-111, NS-115, and others, MIT, July 17, 1945. Div. 11-102-M5

4. *Development and Production of Keyes Type Liquid Oxygen Producers, Final Report for the Period Feb. 1, 1943, to Mar. 31, 1944,* A. C. Shuart, Servel, Inc., June 15, 1944. Div. 11-103.3-M7

5. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for February 1944,* J. H. Rushton and Barnett F. Dodge, OSRD 3523, OEMsr-934, University of Pennsylvania, Apr. 25, 1944. Div. 11-101-M7

6. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for March 1944,* J. H. Rushton and Barnett F. Dodge, OSRD 3652, OEMsr-934, University of Pennsylvania, May 19, 1944. Div. 11-101-M7

7. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for June 1944,* J. H. Rushton, Barnett F. Dodge, and W. L. McCabe, OSRD 3972, OEMsr-934, University of Pennsylvania, Aug. 2, 1944. Div. 11-101-M7

8. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for December 1944*, J. H. Rushton, Barnett F. Dodge, and W. L. McCabe, OSRD 4623, OEMsr-934, University of Pennsylvania. Div. 11-101-M7

9. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for January 1944*, J. H. Rushton, Barnett F. Dodge, and W. L. McCabe, OSRD 4732, OEMsr-934, University of Pennsylvania. Div. 11-101-M7

10. *Final Report of the Central Engineering Laboratory, NDRC, Section 11.1, Oxygen, for March 1943 through June 1945*, John A. Goff and Roy W. Banwell, OSRD 5482, OEMsr-934, NLB-42, NA-106, and others, University of Pennsylvania, June 30, 1945. Div. 11-101-M9

11. *The Joule-Thomson Type Liquid Oxygen Unit* (Supplement I), T. L. Wheeler and Allen Latham, Jr., OEMsr-269, Arthur D. Little, Inc., June 16, 1943. Div. 11-103.3-M3

12. *Shipboard Liquid Oxygen Units, Report to Feb. 3, 1944*, T. L. Wheeler and Allen Latham, Jr., OSRD 3369, OEMsr-269, NA-111, NS-115, Arthur D. Little, Inc., Apr. 6, 1944. Div. 11-103.3-M6

13. *Outline of Proposed Low-Temperature Trailer-Mounted Oxygen Unit for NDRC*, W. F. Giauque, NDCrc-198, University of California, June 15, 1942. Div. 11-102.12-M2

14. *Clark 4-Stage, 3,000-psi Compressor Used in Liquid Oxygen Trailer Unit*, W. F. Giauque, NDrc-198, University of California, Jan. 27, 1944. Div. 11-102.141-M10

15. *Liquid Oxygen Trailer Unit Report to July 25, 1944*, W. F. Giauque, NDCrc-198, OSRD 4141, University of California, Sept. 19, 1944. Div. 11-103.1-M7

16. *Portable Compressor Program Progress Report to Nov. 30, 1942*, Clark Brothers Company, Inc., December 1942. Div. 11-102.141-M5

17. Letter to Earl P. Stevenson, Subject: Portable Compressor Program (includes Elliott Technical Report on Testing of the 200 CFM Elliott-Lysholm Two-Stage Compressor, Dated December 9, 1943), J. N. MacKendrick and A. Van Campen, June 1, 1944. Div. 11-102.141-M12, Div. 11-102.141-M9

18. *Mechanical Oxygen Generating Units & Related Equipment*, J. N. MacKendrick and A. Van Campen, OSRD 4792, Clark Brothers Company, Inc., May 15, 1945. Div. 11-102.1-M8

19. *Oxygen Plant Development Report to February 28, 1945*, Walter E. Lobo, OSRD 4555, M. W. Kellogg Co., Feb. 28, 1945. Div. 11-102-M4

20. *Oxygen Plant 350-450 CFH Gas or Liquid Production*, Wolcott Dennis, June 15, 1943.

21. *Portable Oxygen Unit No. MII-400-AC (NS-116)*, Wolcott Dennis, Jan. 27, 1943.

22. *Oxygen Processes Report to Sept. 1, 1945*, OSRD 5928, Air Reduction Co., Inc., Oct. 1, 1945. Div. 11-103.3-M8

23. *Report on Akerman Liquid Oxygen Converter*, Washington File A-906, Submitted by BuS, Navy Dept., Washington, D.C., on Feb. 16, 1943, (May 19, 1943).

SUPPLEMENTARY

24. *Various Oxygen Producing Units Progress Report, NDRC Contract No. NDCrc-206 with the Air Reduction Co., for Period Nov. 15–Dec. 31, 1943*, Wolcott Dennis, Air Reduction Co., Inc., December 1943. Div. 11-102.1[illegible]

25. *Skid Mounted Oxygen Plant, Progress Report on NDRC Contract No. NDCrc-206*, Wolcott Dennis, Air Reduction Co., Nov. 15, 1943. Div. 11-102.12[illegible]

26. *Various Oxygen Producing Units Monthly Report*, Wolcott Dennis, Air Reduction Co., October 1942. Div. 11-102.1-M4

27. *Monthly Report for Various Oxygen Producing Units*, Wolcott Dennis, Air Reduction Co., September 1942. Div. 11-102.1-M4

28. *Monthly Report for Various Oxygen Producing Units*, Wolcott Dennis, Air Reduction Co., August 1942. Div. 11-102.1-M4

29. *Monthly Report for Various Oxygen Producing Units*, Wolcott Dennis, Air Reduction Co., July 1942. Div. 11-102.1-M4

30. *Monthly Report for Various Oxygen Producing Units*, Wolcott Dennis, Air Reduction Co., June 1942 (dated July 2, 1942). Div. 11-102.1-M4

31. *Report of All Work Done up to June 1, 1942, Toward the Development of: (a) Large Shipboard Oxygen Liquid Unit 4,000 Lbs/Hr; (b) Small Portable Gas Unit 300 Cu Ft/Hr*, Wolcott Dennis, Air Reduction Co.

32. *Report on Tests on Oxygen Rectification Equipment to Feb. 12, 1942*, S. S. Prentiss, OSRD 450.

33. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report Covering Period from 1943 to Jan. 31, 1944*, J. H. Rushton, University of Pennsylvania. Div. 11-101-M7

34. *Processes for the Removal of Carbon Dioxide from the Atmosphere of a Submarine*, Allan P. Colburn and Barnett F. Dodge, University of Pennsylvania, Feb. 20, 1944. Div. 11-105.22-M3

35. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progess Report for April 1944*, J. H. Rushton and W. L. McCabe, OSRD 3760, University of Pennsylvania, June 9, 1944. Div. 11-101-M7

36. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for May 1944*, J. H. Rushton, Barnett F. Dodge, and W. L. McCabe, OSRD 3861, University of Pennsylvania, July 7, 1944. Div. 11-101-M7

37. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for July 1944*, J. H. Rushton, Barnett F. Dodge, and W. L. McCabe, OSRD 4142, University of Pennsylvania, Sept. 19, 1944. Div. 11-101-M7

38. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for August 1944*, J. H. Rushton, Barnett F. Dodge, and W. L. McCabe, OSRD 4207, University of Pennsylvania, Oct. 6, 1944. Div. 11-101-M7

39. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for September 1944*, J. H. Rushton, W. L. McCabe, and Barnett F. Dodge, OSRD 4302, University of Pennsylvania, Nov. 6, 1944. Div. 11-101-M7

40. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for October 1944*, J. H. Rushton, Barnett F. Dodge, and W. L. McCabe, OSRD 4452 University of Pennsylvania, Dec. 13, 1944. Div. 11-101-M7

41. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for November 1944*, J. H. Rushton, Barnett F. Dodge, and W. L. McCabe, OSRD 4516, University of Pennsylvania, Dec. 30, 1944. Div. 11-101-M7

42. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for February 1945*, J. H. Rushton, Barnett F. Dodge, and W. L. McCabe, OSRD 4879, University of Pennsylvania, Mar. 30, 1945. Div. 11-101-M7

43. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for March 1945*, W. L. McCabe, OSRD 5040, University of Pennsylvania, Apr. 30, 1945. Div. 11-101-M7

44. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for April 1945*, W. L. McCabe, OSRD 5153, University of Pennsylvania, May 31, 1945. Div. 11-101-M7

45. *Conference on Small Oxygen Units*, C. C. Furnas, M. W. Kellogg Company, July 13, 1942. Div. 11-102.11-M1

46. *Comparison of M-2 and MIT Oxygen Producing Units*, George T. Skaperdas, Oct. 5, 1942.

47. *Mobile Oxygen Units Liquid Air Fractionation Systems*, Walter E. Lobo, M. W. Kellogg Company, Feb. 3, 1943. Div. 11-103.4-M3

48. *Observation of Air Reduction in NDRC Skid Unit on December 6, 1943*, George T. Skaperdas, December 1943. Div. 11-102.12-M6

49. *The Development of a Low-Temperature Engine Compressor Rectifier Unit for the Separation of Oxygen from Air*, Frederick G. Keyes and S. C. Collins, Sept. 12, 1941. Div. 11-102.1-M1

50. *Airplane Oxygen Unit*, Frederick G. Keyes, NDCrc-182, MIT, June 27, 1942. Div. 11-102.111-M1

51. *Report on Airplane Oxygen Unit, Progress Report on the Possibility of Using the Phenomenon of Heat Transmission at Low Pressures as a Means of Detecting and Determining Gaseous Compositions*, data obtained by D. A. Williams, Aug. 8, 1942.

52. *Instructions for Operating the Mond-Ricardo British Oxygen-Gas Producer, Appendix of Memoranda Pertaining to Its Construction, Servicing, and Maintenance*, Frederick G. Keyes, MIT, Sept. 28, 1942. Div. 11-102.111-M3

53. *Liquid Oxygen Pump*, Frederick G. Keyes, NDCrc-182, MIT, Nov. 17, 1943. Div. 11-103.2-M2

54. *Operating Instructions for MIT Model S-Unit for Producing Liquefied Oxygen for Respiratory Use on Submarines and Other Purposes*, prepared by D. A. Williams, submitted by Frederick G. Keyes, Mar. 24, 1944.

55. *Report of Progress under Contract OEMsr-654*, J. F. Pritchard, J. F. Pritchard Company, Dec. 14, 1942. Div. 11-103.3-M2

56. *Instrument Instructions—Liquid Oxygen Plant—M-6*, J. F. Pritchard Company.

57. *Production Progress of Oxygen Producing Unit, Monthly Report from March 15 to April 15, 1943*, R. R. Enders, NDCrc-830, Servel, Inc., April 1943. Div. 11-101-M8

58. *Report on Liquid Oxygen, May 1 to June 30, 1941*, W. F. Giauque, University of California.

59. *Informal Comments Requested by the M. W. Kellogg Co. on Provisional Design of Oxygen Units*, W. F. Giauque, NDCrc-198, University of California, May 15, 1942. Div. 11-102.12-M1

60. *Instructions and Flow Sheet for Giauque Unit*, in letter to J. H. Rushton from W. F. Giauque, Apr. 28, 1944.

61. *Review of Oxygen Program for 1942, Including Bi-Monthly Report for Dec. 1942 and Jan. 1943*, for meeting with NDRC Reviewing Committee, Feb. 13, 1943.

62. *Résumé of Oxygen Program*, Section 11.1, NDRC, Jan. 12, 1944.

63. *Minutes of Meeting on Field Generation of Oxygen Held in Pentagon Bldg., Washington, D.C., Apr. 16, 1943*, from Maj. Gen. C. C. Williams.

64. *Oxygen Units under Development by the NDRC*, S. S. Prentiss, Jan. 1, 1943. Div. 11-101-M6

65. *The Oxygen Technical Committee Meeting*, Aug. 20, 1942. Div. 11-101-M4

66. *Oxygen Units under Development by the NDRC*, S. S. Prentiss, Aug. 14, 1942. Div. 11-101-M5

67. *Information on the Mark I Mond Oxygen Separator*, Letter from T. R. Hogness to H. M. Chadwell, Washington File B-12134, Aug. 5, 1942.

68. *Abstract of Description and Tests on Mond-Ricardo Oxygen Plant*, March 1942.

69. *Experimental Small Oxygen Compressor*, Report No. 1207, Washington File B-3833, Ricardo & Co., Oct. 21, 1943.

70. *Underground Oxygen Plant Located at Wittring, France*, Washington File B-4791, Mar. 21, 1945.

71. *German Liquid Oxygen Plant at Liege*, Oct. 5, 1944.

Chapter 5

1. Letter to C. C. Furnas, Subject: Portable Compressor Program Progress Report for Period from Early February to April 15, 1942, J. N. MacKendrick, Clark Brothers Company, Inc., April 15, 1942. Div. 11-102.141-M1

2. Letter to C. C. Furnas, Subject: Portable Compressor Program Progress Report for Period April 15 to May 15, 1942, J. N. MacKendrick, Clark Brothers Company, Inc., May 15, 1942. Div. 11-102.141-M2

3. Letter to C. C. Furnas, Subject: Portable Compressor Program, J. N. MacKendrick, Clark Brothers Company, Inc., Sept. 19, 1942. Div. 11-102.141-M4
4. *Portable Compressor Program Progress Report to November 30, 1942*, Clark Brothers Company, Inc., December 1942. Div. 11-102.141-M5
5. Letter to Earl P. Stevenson, Subject: Portable Compressor Program, J. N. MacKendrick and A. Van Campen, Clark Brothers Company, Inc., June 1, 1943. Div. 11-102.141-M6
6. Letter to Earl P. Stevenson, Subject: Portable Compressor Program, J. N. MacKendrick and A. Van Campen, Clark Brothers Company, Inc., July 20, 1943. Div. 11-102.141-M7
7. Letter to Earl P. Stevenson, Subject: Portable Compressor Program, J. N. MacKendrick and A. Van Campen, Clark Brothers Company, Inc., Sept. 25, 1943. Div. 11-102.141-M8
8. *Clark Two-Stage 5"x3"x3½" Dri-Oxygen Compressor*, Clark Brothers Company, Inc., Oct. 15, 1943. Div. 11-102.142-M1
9. Letter to Earl P. Stevenson, Subject: Portable Compressor Program (includes Elliott Mechanical Report on Testing of the 200 CFM Elliott-Lysholm Two-Stage Compressor, dated Dec. 9, 1943), J. N. MacKendrick and A. Van Campen, Clark Brothers Company, Inc., June 1, 1944. Div. 11-102.141-M12, Div. 11-102.141-M9
10. Letter to Earl P. Stevenson, Subject: Portable Compressor Program, J. N. MacKendrick and A. Van Campen, Clark Brothers Company, Inc., Feb. 15, 1944. Div. 11-102.141-M11
11. *Mechanical Oxygen Generating Units and Related Equipment*, J. N. MacKendrick and A. Van Campen, OSRD 4792, Clark Brothers Company, Inc., May 15, 1945. Div. 11-102.1-M8
12. *Progress Report*, Walter E. Lobo, Clark Brothers Company, Inc., March 19, 1942.
13. *Progress Report, September 29 to November 11, 1943*, Walter E. Lobo, Clark Brothers Company, Inc., Nov. 18, 1943.
14. *Progress Report, November 11 to December 31, 1942*, Walter E. Lobo, Clark Brothers Company, Inc., Jan. 3, 1944.
15. *Oxygen Plant Development—Report to February 28, 1945*, Walter E. Lobo, OSRD 4555, M. W. Kellogg Company, Feb. 28, 1945. Div. 11-102-M4
16. *First Progress Report, Yale University, Small Portable Plants for the Production of Liquid Oxygen, June 14, 1941*, Barnett F. Dodge, Dodge Serial No. 45, issued June 27, 1941.
17. *The Production of Liquid Oxygen*, Barnett F. Dodge and Harding Bliss, NDCrc-80, Yale University, Aug. 1, 1941. Div. 11-103.1-M3
18. Letter to S. S. Prentiss, Subject: Expander Casing and Compressor, J. R. McDermet, Elliott Company, Aug. 7, 1942. Div. 11-102.13-M2
19. *The Development of 1700-CFM Low Temperature Expander, Progress Report for Period July 1 to August 15, 1942*, Judson S. Swearingen, Elliott Company, Aug. 19, 1942. Div. 11-102.13-M1
20. *The Development of 1700-CFM Low Temperature Expander, Progress Report for Period August 16 to September 15, 1942*, Judson S. Swearingen, Elliott Company, Sept. 16, 1942. Div. 11-102.13-M1
21. *Small Hapeg Compressors, Report No. 14*, Judson S. Swearingen, Elliott Company, Sept. 19, 1942. Div. 11-102.141-M3
22. *Development of 1700-CFM Low Temperature Expander for M-5 Unit, Feb. 15 to Mar. 15, 1943*, Judson S. Swearingen, Elliott Company. Div. 11-102.13-M1
23. *The Development of a Low Temperature Engine-Compressor-Rectifier Unit for the Separation of Oxygen from Air*, Frederick G. Keyes and S. C. Collins, Sept. 12, 1941. Div. 11-102.1-M1
24. *Special Report No. 4, Compressors, Expansion Engine, Interchangers, Rectifiers*, F. G. Keyes, Apr. 15, 1942.
25. *A Light-Weight, Automatic, Mechanical Oxygen Generator Issued June 19, 1944*, S. C. Collins and Howard O. McMahon, May 31, 1944. Div. 11-102.111-M7
26. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for March 1944*, J. H. Rushton and Barnett F. Dodge, OSRD 3652, University of Pennsylvania. Div. 11-101-M7
27. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for April 1944*, J. H. Rushton and W. L. McCabe, OSRD 3760, University of Pennsylvania, June 9, 1944. Div. 11-101-M7
28. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for June 1944*, J. H. Rushton, Barnett F. Dodge, and W. L. McCabe, OSRD 3972, University of Pennsylvania, Aug. 2, 1944. Div. 11-101-M7
29. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for July 1944*, J. H. Rushton, Barnett F. Dodge, and W. L. McCabe, OSRD 4142, University of Pennsylvania, Sept. 19, 1944. Div. 11-101-M7
30. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for October 1944*, J. H. Rushton, Barnett F. Dodge, and W. L. McCabe, OSRD 4452, University of Pennsylvania, Dec. 13, 1944. Div. 11-101-M7
31. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for December 1944*, J. H. Rushton, W. L. McCabe, and Barnett F. Dodge, OSRD 4623, University of Pennsylvania, Jan. 24, 1945. Div. 11-101-M7
32. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for January 1945*, J. H. Rushton, W. L. McCabe, and Barnett F. Dodge, OSRD 4732, University of Pennsylvania, Mar. 3, 1945. Div. 11-101-M7

33. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for March 1945*, W. L. McCabe, OSRD 5040, University of Pennsylvania, Apr. 30, 1945. Div. 11-101-M7
34. *Final Report of Central Engineering Laboratory, University of Pennsylvania for Period March 1943 through June 30, 1945*, John A. Goff and Roy W. Banwell, OSRD 5482, University of Pennsylvania, June 30, 1945. Div. 11-101-M9
35. *Clark Four-Stage, 3000-psi Compressor used in Liquid Oxygen Trailer Unit*, W. F. Giauque, NDCrc-198, University of California, Jan. 27, 1944. Div. 11-102.141-M10
36. *Liquid Oxygen Trailer Unit, Report to July 25, 1944*, W. F. Giauque, NDCrc-198, OSRD 4141, University of California, Sept. 19, 1944. Div. 11-103.1-M7
37. *Tests of Performance of the Collins-Type Expansion Engine Built by Clark Bros. Co., Inc., Report to Jan. 26, 1944*, J. G. Ashton, OSRD 3482, Pennsylvania State College, Apr. 14, 1944. Div. 11-102.13-M3
38. *Oxygen Processes*, OSRD 5928, Air Reduction Co., Oct. 1, 1945.

SUPPLEMENTARY

39. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for 1943 to Jan. 21, 1944*, J. H. Rushton, University of Pennsylvania. Div. 11-101-M7
40. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for February 1944*, J. H. Rushton and Barnett F. Dodge, OSRD 3523, University of Pennsylvania, Apr. 25, 1944. Div. 11-101-M7
41. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for May 1944*, J. H. Rushton, Barnett F. Dodge, and W. L. McCabe, OSRD 3961, University of Pennsylvania, July 7, 1944. Div. 11-101-M7
42. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for September 1944*, J. H. Rushton, Barnett F. Dodge, and W. L. McCabe, OSRD 4302, University of Pennsylvania, Nov. 6, 1944. Div. 11-101-M7
43. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for February 1945*, J. H. Rushton, W. L. McCabe, and Barnett F. Dodge, OSRD 4879, University of Pennsylvania, Mar. 30, 1945. Div. 11-101-M7
44. *The Development of 1700-CFM Low Temperature Expander, Monthly Progress Report for Sept. 16 to Oct. 15, 1942*, Judson S. Swearingen, Elliott Company, Oct. 16, 1942. Div. 11-102.13-M1
45. *The Development of 1700-CFM Low Temperature Expander, Monthly Progress Report for October 15 to November 15, 1942*, Judson S. Swearingen, Elliott Company, Nov. 18, 1942. Div. 11-102.13-M1
46. *The Development of 1700-CFM Low Temperature Expander, Monthly Progress Report for November 16 to December 15, 1942*, Judson S. Swearingen, Elliott Company. Div. 11-102.13-M1
47. *The Development of 1700-CFM Low Temperature Expander, Monthly Progress Report for Dec. 15, 1942 to Jan. 15, 1943*, Judson S. Swearingen, Elliott Company. Div. 11-102.13-M1
48. *The Development of 1700-CFM Low Temperature Expander, Monthly Progress Report for Jan. 15 to Feb. 15, 1943*, Judson S. Swearingen, Elliott Company. Div. 11-102.13-M1
49. *The Development of 1700-CFM Low Temperature Expander, Monthly Progress Report for Mar. 15 to Apr. 15, 1943*, Judson S. Swearingen, Elliott Company. Div. 11-102.13-M1
50. *The Development of 1700-CFM Low Temperature Expander, Monthly Progress Report for Apr. 15 to May 15, 1943*, Judson S. Swearingen, Elliott Company. Div. 11-102.13-M1
51. *The Development of 1700-CFM Low Temperature Expander, Monthly Progess Report for May 15, 1943 to June 15, 1943*, Judson S. Swearingen, Elliott Company. Div. 11-102.13-M1
52. *The Development of 1700-CFM Low Temperature Expander, Monthly Progress Report for June 15 to July 15, 1943*, Judson S. Swearingen, Elliott Company, July 23, 1943. Div. 11-102.13-M1
53. *The Development of 1700-CFM Low Temperature Expander, Monthly Progress Report, Aug. 15 to Sept. 15, 1943*, Judson S. Swearingen, Elliott Company, Sept. 22, 1943. Div. 11-102.13-M1
54. *The Development of 1700-CFM Low Temperature Expander, Monthly Progress Report, Sept. 15 to Oct. 15, 1943*, Judson S. Swearingen, Elliott Company, Oct. 22, 1943. Div. 11-102.13-M1
55. *The Development of 1700-CFM Low Temperature Expander, Monthly Progress Report, Oct. 15 to Nov 15, 1943*, Judson S. Swearingen, Elliott Company, Nov. 22, 1943. Div. 11-102.13-M1
56. *The Development of 1700-CFM Low Temperature Expander, Monthly Progress Report, Nov. 15, 1943 to Dec. 15, 1943*, Judson S. Swearingen, Elliott Company, Dec. 21, 1943. Div. 11-102.13-M1
57. *Various Oxygen Producing Units, Monthly Progress Report for Apr. 23, 1942*, Walter E. Lobo, M. W. Kellogg Co. Div. 11-102-M1
58. *Various Oxygen Producing Units, Monthly Progress Report for May 15, 1942*, Walter E. Lobo, M. W. Kellogg Co. Div. 11-102-M1
59. *Various Oxygen Producing Units, Monthly Progress Report for June 15 to July 15, 1942*, Walter E. Lobo, M. W. Kellogg Co. Div. 11-102-M1
60. *Various Oxygen Producing Units, Monthly Progress Report for July 15 to Aug. 15, 1942*, Walter E. Lobo, M. W. Kellogg Co. Div. 11-102-M1
61. *Various Oxygen Producing Units, Monthly Progress Report for Aug. 15 to Sept. 15, 1942*, Walter E. Lobo, M. W. Kellogg Co. Div. 11-102-M1
62. *Various Oxygen Producing Units, Monthly Progress Report for Sept. 15 to Oct. 15, 1942*, Walter E. Lobo, M. W. Kellogg Co. Div. 11-102-M1

63. *Various Oxygen Producing Units, Monthly Progress Report for Oct. 15 to Nov. 15, 1942*, Walter E. Lobo, M. W. Kellogg Co. Div. 11-102-M1

64. *Various Oxygen Producing Units, Monthly Progress Report for Nov. 15 to Dec. 15, 1942*, Walter E. Lobo, M. W. Kellogg Co. Div. 11-102-M1

65. *Various Oxygen Producing Units, Monthly Progress Report for Dec. 15, 1942 to Jan. 15, 1943*, Walter E. Lobo, M. W. Kellogg Co. Div. 11-102-M1

66. *Mobile Oxygen Units Liquid Air Fractionation Systems*, Walter E. Lobo, M. W. Kellogg Company, Feb. 3, 1943. Div. 11-103.4-M3

67. *Various Oxygen Producing Units, Monthly Progress Report for Jan. 15 to Feb. 15, 1943*, Walter E. Lobo, M. W. Kellogg Co. Div. 11-102-M1

68. *Various Oxygen Producing Units, Monthly Progress Report for Feb. 15 to Mar. 15, 1943*, Walter E. Lobo, M. W. Kellogg Co. Div. 11-102-M1

69. *Various Oxygen Producing Units, Monthly Progress Report for Mar. 15 to Apr. 15, 1943*, Walter E. Lobo, M. W. Kellogg Company. Div. 11-102.1-M2

70. *Various Oxygen Producing Units, Monthly Progress Report for Apr. 15 to May 31, 1943*, Walter E. Lobo, M. W. Kellogg Co. Div. 11-102.1-M2

71. *Various Oxygen Producing Units, Monthly Progress Report for June 1 to July 1, 1943*, Walter E. Lobo, M. W. Kellogg Company. Div. 11-102.1-M2

72. *Various Oxygen Producing Units, Monthly Progress Report for July 1 to 27, 1943*, Walter E. Lobo, M. W. Kellogg Company. Div. 11-102.1-M2

73. *Various Oxygen Producing Units, Monthly Progress Report for July 27 to Aug. 26, 1943*, Walter E. Lobo, M. W. Kellogg Company. Div. 11-102.1-M2

74. *Various Oxygen Producing Units, Monthly Progress Report for Aug. 27 to Sept. 28, 1943*, Walter E. Lobo, M. W. Kellogg Company. Div. 11-102.1-M2

75. *Low-Pressure Mobile Gaseous Oxygen Units Developed for NDRC at Olean, N.Y.*, Clark Bros. Co. Inc., and the M. W. Kellogg Co., Oct. 29, 1943. Div. 11-102.12-M4

76. Report dated November 1, 1943, summarizing the work on the M-2R unit at O'Fallon, J. Broadbent.

77. *Performance of M-7AT Radiators*, Eugene Miller, M. W. Kellogg Company, Apr. 16, 1945. Div. 11-102.141-M13

Chapter 6

1. *Progress Report, Clark Bros. Co., Inc., Portable Compressor Program*, to C. C. Furnas from J. N. MacKendrick, December 24, 1942.

2. *Mechanical Oxygen Generating Units and Related Equipment*, J. N. MacKendrick and A. Van Campen, OSRD 4792, Clark Bros. Co., Inc., May 15, 1945. Div. 11-102.1-M8

3. *Liquid Oxygen Pump and Vaporizer, Report to May 15, 1945*, T. L. Wheeler and Allen Latham, Jr., OSRD 5152, Arthur D. Little, Inc., May 31, 1945. Div. 11-103.2-M3

4. *Liquid Oxygen Pump*, Frederick G. Keyes, ND... MIT, Nov. 17, 1943. Div. 11-1...

5. *A Light-Weight, Automatic, Mechanical Oxygen ... erator*, Report to May 31, 1944, S. C. Collins and ... ard O. McMahon, OSRD-3800, MIT, June 19, 19... Div. 11-102...

6. *Oxygen Generating Equipment, Report to June 3...*, Frederick G. Keyes, OSRD-5329, NDCrc-182, ... July 17, 1945. Div. 11-1...

7. *Final Report of Central Engineering Laboratory, ... versity of Pennsylvania, for Period from March ... through June 1945*, John A. Goff and Roy W. Ba... OSRD 5482, University of Pennsylvania, June 30, ... Div. 11-10... M9

8. *Liquid Oxygen Trailer Unit*, Report to July 25, ... W. F. Giauque, OSRD 4141, NDCrc-198, University of California, Sept. 19, 1944. Div. 11-103... M7

Chapter 7

1. *Some Consideration on the Removal of Water and Carbon Dioxide in Reversing Exchangers*, Sept. 3, 1943. Div. 11-104.13-M8

2. *History of the Development of Heat Exchangers for Low-Pressure Mobile Oxygen Units*, Walter E. Lobo, M. W. Kellogg Company, Oct. 4, 1943. Div. 11-104.13-M5

3. *History of the Development of Heat Exchangers for Low-Pressure Mobile Oxygen Units*, Walter E. Lobo and George T. Skaperdas, M. W. Kellogg Company, Oct. 9, 1943. Div. 11-104.13-M6

4. *Liquid Air Fractionation, Progress Report to May 15, 1944*, Walter E. Lobo and B. Williams, OSRD 3768, M. W. Kellogg Company, June 13, 1944. Div. 11-103.4-M5

5. *Heat Transfer and Pressure Drop in Collins Exchanger, Report to Aug. 15, 1944*, P. R. Trumpler, OSRD 4143, M. W. Kellogg Company, Sept. 19, 1944. Div. 11-104.13-M7

6. *Oxygen Plant Development, Report to February 28, 1945*, Walter E. Lobo, OSRD 4555, M. W. Kellogg Company, Feb. 28, 1945. Div. 11-102-M4

7. *Preliminary Results of Tests on Regenerators*, Harding Bliss, Yale University, Aug. 1, 1942. Div. 11-104.13-M2

8. *Regenerators, Progress Report Covering Period from August 1, 1942 to March 15, 1943*, Harding Bliss, OSRD 1443, Yale University, May 21, 1943. Div. 11-104.13-M4

9. *Experimental Study of Special Equipment for Use in Low Temperature Cycles for the Production of Liquid and Gaseous Oxygen, Report to July 1, 1945*, Hard... Bliss and Barnett F. Dodge, OSRD 6302, Yale University, Nov. 7, 1945. Div. 11-103.4-...

10. *A Light-Weight, Automatic, Mechanical Oxygen Generator*, S. C. Collins and Howard O. McMahon, OS... 3800, NDCrc-182, Service Projects AC-12, NS-... CE-29, MIT, June 19, 1944. Div. 11-102.111-...

11. *Oxygen Generating Equipment, Report to June 30, ...* Frederick G. Keyes, OSRD 5329, MIT, July 17, 194... Div. 11-102...

12. *Report of Heat Transfer and Design of Refrigeration Evaporators for the NDRC*, W. F. Giauque, Mar. 1, 1942.

13. *Low Temperature Heat Interchangers*, W. F. Giauque, University of California, Apr. 19, 1943. Div. 11-104.13-M3

14. *Liquid Oxygen Trailer Unit, Report to July 25, 1944*, W. F. Giauque, OSRD 4141, NDCrc-198, University of California, Sept. 19, 1944. Div. 11-103.1-M7

15. *Final Report of Central Engineering Laboratory, for Period March 1943 through June 1945*, John A. Goff and Roy W. Banwell, OSRD 5482, OEMsr-934, University of Pennsylvania, June 30, 1945. Div. 11-101-M9

16. *Oxygen Processes, Report to September 1, 1945*, OSRD 5982, NDCrc-206, Air Reduction Company, Inc., Oct. 1, 1945. Div. 11-103.3-M8

17. *Shipboard Liquid Oxygen Units, Report to February 3, 1944*, T. L. Wheeler and Allen Latham, Jr., OSRD 3369, Arthur D. Little Inc., Apr. 6, 1944. Div. 11-103.3-M6

18. *Tests of Performance of Portable Unit Columns for Air Rectification, Final Report to January 6, 1944*, J. G. Aston, OSRD 3699, Pennsylvania State College, May 29, 1944. Div. 11-104.12-M4

SUPPLEMENTARY

1. *Progress Report, Semi-Portable Oxygen Unit, M-6 Expander and Unit, November 15 to December 31, 1943*, W. Dennis.

2. *Monthly Progress Report 1943 to January 31, 1944*, J. H. Rushton.

3. *Comparison of M-2 and MIT Oxygen Producing Units*, M. W. Kellogg Company, George T. Skaperdas, Oct. 5, 1942.

4. *Mobile Oxygen Units Liquid Air Fractionation Systems*, Walter E. Lobo, M. W. Kellogg Company, Feb. 3, 1943. Div. 11-103.4-M3

5. *Heat Transfer Rates in Collins Exchanger Packings*, July 24, 1943.

6. *Low-Pressure Mobile Gaseous Oxygen Units Developed for NDRC at Olean, N.Y.*, Clark Bros. Co. Inc. and M. W. Kellogg Company, Oct. 29, 1943. Div. 11-102.12-M4

7. Report Summarizing the Work on the M-2R Unit at O'Fallon from M. W. Kellogg Company, J. Broadbent, Nov. 1, 1943.

8. *Observation of Air Reduction in NDRC Skid Unit on December 6, 1943*, George T. Skaperdas, December 1943. Div. 11-102.12-M6

9. *Visit to Air Reduction Sales Company, December 15 and 16, 1943*, George T. Skaperdas, December 1943. Div. 11-102.1-M6

10. *Special Report No. 2, Heat Interchangers for Gases*, S. C. Collins, Mar. 9, 1942. Div. 11-104.13-M1

11. *Special Report No. 3, Alternating Flow Scrubber-Heat Exchanger*, S. C. Collins. Div. 11-104.13-M1

12. *Special Report No. 4, Compressors, Expansion Engine, Interchangers, Rectifiers*, Frederick G. Keyes, Apr. 15, 1942.

Chapter 8

1. *Liquid Air Fractionation, Progress Report to May 15, 1944*, Walter E. Lobo and B. Williams, OSRD 3768, M. W. Kellogg Company, June 13, 1944. Div. 11-103.4-M5

2. *Technical Data with Respect to the Properties of Air*, Walter E. Lobo, OSRD 4206, M. W. Kellogg Company, Oct. 6, 1944. Div. 11-102.15-M2

3. *Oxygen Plant Development, Report to February 28, 1945*, Walter E. Lobo, OSRD 4555, M. W. Kellogg Company, Feb. 28, 1945. Div. 11-102-M4

4. *A Light-Weight, Automatic, Mechanical Oxygen Generator to May 31, 1944*, S. C. Collins and Howard O. McMahon, OSRD 3800, NDCrc-182, Service Projects AC-12, NS-116, CE-29, MIT, June 19, 1944. Div. 11-102.111-M7

5. *Oxygen Generating Equipment, Report to June 30, 1945*, Frederick G. Keyes, OSRD 5329, NDCrc-182, MIT, July 17, 1945. Div. 11-102-M5

6. *Résumé of Oxygen Program, Section 11.1, NDRC*, Jan. 12, 1944.

7. *Final Report, Liquid Oxygen Trailer Unit, Report to July 25, 1944*, W. F. Giauque, OSRD 4141, NDCrc-198, University of California, Sept. 19, 1944. Div. 11-103.1-M7

8. *The Truck Unit for Air Rectification Designed and Being Built by W. F. Giauque at the University of California*, University of California, Feb. 8, 1943. Div. 11-103.4-M8

9. *Tray Calculations Made at the Pennsylvania State College*, J. G. Aston and June Pfister, Pennsylvania State College, Feb. 15, 1943. Div. 11-104.11-M3

10. *Heats of Vaporization O_2-N_2*, J. G. Aston, S. C. Schumann, and others, OSRD 1507, M. W. Kellogg Company, June 10, 1943.

11. *Tests of Performance of Portable Unit Columns for Air Rectification*, Final Report to January 6, 1944, J. G. Aston, OSRD 3699, Pennsylvania State College, May 29, 1944. Div. 11-104.12-M4

12. *Calculation of the Number of Plates in an Air Rectification Tower*, Report to January 25, 1944, J. G. Aston, OSRD 3524, Pennsylvania State College, Apr. 25, 1944. Div. 11-104.11-M4

13. *Vapor-Liquid Equilibrium for the System Oxygen-Nitrogen-Argon*, J. G. Aston, OSRD 4493, Contracts OEMsr-685 and OEMsr 934, Pennsylvania State College, Dec. 7, 1944. Div. 11-103.4-M6

14. *Rectification of Air in a Two-Inch Packed Column*, Barnett F. Dodge, Report No. 365 to August 6, 1942, OSRD 876, Yale University, Sept. 17, 1942. Div. 11-104.11-M2

15. *Experimental Study of Special Equipment for Use in Low Temperature Cycles for the Production of Liquid and Gaseous Oxygen, Report to July 1, 1945*, Harding Bliss and Barnett F. Dodge, OSRD 6302, Yale University, Nov. 7, 1945. Div. 11-103.4-M7

16. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for May 1944,* J. H. Rushton, Barnett F. Dodge, and W. L. McCabe, OSRD 3861, University of Pennsylvania, July 7, 1944. Div. 11-101-M7
17. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for June 1944,* J. H. Rushton, Barnett F. Dodge, and W. L. McCabe, OSRD 3972, University of Pennsylvania, Aug. 2, 1944. Div. 11-101-M7
18. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for August 1 to 31, 1944,* J. H. Rushton, Barnett F. Dodge, and W. L. McCabe, OSRD 4207, University of Pennsylvania, Oct. 6, 1944. Div. 11-101-M7
19. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for September 1 to 30, 1944,* J. H. Rushton, Barnett F. Dodge, and W. L. McCabe, OSRD 4302, University of Pennsylvania, Nov. 6, 1944. Div. 11-101-M7
20. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for October 1 to October 31, 1944,* J. H. Rushton, Barnett-F. Dodge, and W. L. McCabe, OSRD 4452, University of Pennsylvania, Dec. 13, 1944. Div. 11-101-M7
21. *Final Report of Central Engineering Laboratory, University of Pennsylvania for the Period March 1943 through June 1945,* John A. Goff and Roy W. Banwell, OSRD 5482, University of Pennsylvania, June 30, 1945. Div. 11-101-M9
22. *Report of All Work Done up to June 1, 1942 Toward the Development of: (a) Large Shipboard Oxygen Liquid Unit 4000 Lb/Hr; (B) Small Portable Gas Unit 300 Cu Ft/Hr,* Wolcott Dennis.
23. *Tests on Oxygen Rectification Equipment Report No. 206 to February 12, 1942,* S. S. Prentiss, OSRD 450, Feb. 12, 1942. Div. 11-104.1-M1
24. *Oxygen Processes, Report to Sept. 1, 1945,* NDCrc-206, OSRD 5928, Air Reduction Company, Inc., Oct. 1, 1945. Div. 11-103.3-M8

SUPPLEMENTARY

1. *Conference on Small Oxygen Units,* C. C. Furnas, M. W. Kellogg Company, July 13, 1942. Div. 11-102.11-M1
2. *Comparison of M-2 and MIT Oxygen Producing Units,* M. W. Kellogg Company, G. T. Skaperdas, Oct. 5, 1942.
3. *Mobile Oxygen Units: Liquid Air Fractionation Systems,* Walter E. Lobo, M. W. Kellogg Company, Feb. 3, 1943. Div. 11-103.4-M3
4. *Oxygen Project, NDCrc-182: Rectifiers, Special Report No. 1,* Frederick G. Keyes, MIT, Feb. 27, 1942. Div. 11-104.1-M2
5. *Special Report No. 12, Oxygen Producer, Designed and Built by S. C. Collins,* Frederick G. Keyes, Sept. 25, 1942.
6. Letter to Walter E. Lobo from J. G. Ashton dated January 4, 1942 on data on the Stedman packing.
7. *Monthly Report for Period Ending June 30, 1942,* J. G. Aston.
8. *Progress Report for Month Ending July 31, 1942,* J. G. Aston.
9. *Monthly Report for August 1942,* J. G. Aston.
10. *Monthly Report for September 1942,* J. G. Aston.
11. *Monthly Report for October 1942,* J. G. Aston.
12. *Monthly Report for November 1942,* J. G. Aston.
13. *Monthly Report for December 1942,* J. G. Aston.
14. *Progress Report for January and February 1943,* J. G. Aston.
15. *Monthly Report for March 1943,* J. G. Aston.
16. *Monthly Report for April 1943,* J. G. Aston.
17. *Monthly Report for May 1943,* J. G. Aston.
18. *Monthly Report for June 1943,* J. G. Aston.
19. *Monthly Report for July 1943,* J. G. Aston.
20. *Monthly Report for August 1943,* J. G. Aston.
21. *Monthly Report for September 1943,* J. G. Aston.
22. *Tentative Outline of Program of Experimental Investigations for NDRC and Present Status of This Work,* Barnett F. Dodge, Mar. 18, 1942.
23. *Review of Program of Experimental Work for NDRC,* Yale University, Sept. 8, 1942. Div. 11-104-M1
24. Sherwood, Shepley & Holloway, *Ind. Eng. Chem.,* 30, 1938, p. 765.

Chapter 9

1. *The Investigations Carried Out under Contract No. OEMsr-355 with Yale University,* Barnett F. Dodge, Yale University, June 15, 1942. Div. 11-101-M3
2. *The Investigations Carried Out under Contract No. OEMsr-355 with Yale University,* Barnett F. Dodge, Yale University, Aug. 15, 1942. Div. 11-101-M3
3. *Review of Program of Experimental Work for NDRC,* Barnett F. Dodge, Yale University, Sept. 8, 1942. Div. 11-104-M1
4. *The Investigations Carried Out under Contract No. OEMsr-355 with Yale University,* Barnett F. Dodge, Yale University, Sept. 15, 1942. Div. 11-101-M3
5. *The Investigations Carried Out under Contract No. OEMsr-355 with Yale University,* Barnett F. Dodge, Yale University, Oct. 15, 1942. Div. 11-101-M3
6. *The Investigations Carried Out under Contract No. OEMsr-355 with Yale University,* Barnett F. Dodge, Yale University, Nov. 15, 1942. Div. 11-101-M3
7. *The Investigations Carried Out under Contract No. OEMsr-355 with Yale University,* Barnett F. Dodge, Yale University, Dec. 15, 1942. Div. 11-101-M3
8. *A Colorimetric Method for the Determination of Traces of Carbon Dioxide in Air, Progress Report to February 8, 1943,* Norman A. Spector, OSRD 1426, Yale University, May 17, 1943. Div. 11-105 M1
9. *The Investigations Carried Out under Contract No. OEMsr-355 with Yale University,* Barnett F. Dodge, Yale University, Feb. 15, 1943. Div. 11-101-M3
10. *The Investigations Carried Out under Contract No. OEMsr-355 with Yale University,* Barnett F. Dodge, Yale University, Mar. 15, 1943. Div. 11-101-M3

11. *The Investigations Carried Out under Contract No. OEMsr-355 with Yale University,* Barnett F. Dodge, Yale University, Apr. 15, 1943. Div. 11-101-M3
12. *The Investigations Carried Out under Contract No. OEMsr-355 with Yale University,* Barnett F. Dodge, Yale University, May 15, 1943. Div. 11-101-M3
13. *The Investigations Carried Out under Contract No. OEMsr-355 with Yale University,* Barnett F. Dodge, Yale University, June 15, 1943. Div. 11-101-M3
14. *The Removal of Carbon Dioxide from Atmospheric Air, Progress Report to November 1, 1944,* Norman A. Spector, OSRD 4340, Yale University, Nov. 14, 1944. Div. 11-105.22-M4
15. *Experimental Study of Special Equipment for Use in Low Temperature Cycles for the Production of Liquid and Gaseous Oxygen, Report to July 1, 1945,* Harding Bliss and Barnett F. Dodge, OSRD 6302, Yale University, Nov. 7, 1945. Div. 11-103.4-M7
16. *Drying Air with Activated Granular Adsorbents,* J. F. Skelly, M. W. Kellogg Company, April 3, 1943. Div. 11-105.21-M1
17. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for February 1944,* J. H. Rushton, Barnett F. Dodge, and others, OSRD 3523, University of Pennsylvania, Apr. 25, 1944. Div. 11-101-M7
18. *Processes for the Removal of Carbon Dioxide from the Atmosphere of a Submarine,* Allan P. Colburn and Barnett F. Dodge, University of Pennsylvania, Feb. 20, 1944. Div. 11-105.22-M3
19. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for August 1944,* J. H. Rushton, Barnett F. Dodge, and others, OSRD 4207, University of Pennsylvania, Aug. 31, 1944. Div. 11-101-M7
20. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for September 1944,* J. H. Rushton, Barnett F. Dodge, and others, OSRD 4302, University of Pennsylvania. Div. 11-101-M7
21. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for October 1944,* J. H. Rushton, Barnett F. Dodge, and others, OSRD 4452, University of Pennsylvania. Div. 11-101-M7
22. *The Removal of Traces of Acetylene and Other Hydrocarbons from Air,* J. G. Aston and T. A. Geissman, OSRD 4844, University of Pennsylvania, Mar. 5, 1945. Div. 11-105.23-M1
23. *Monthly Progress Report, March 1 to 31, 1945,* W. L. McCabe, OSRD 5040.
24. *Final Report of Central Engineering Laboratory, University of Pennsylvania, for the Period March 1943 through June 1945,* John A. Goff and Roy W. Banwell, OSRD 5482, OEMsr-934, Service Project No. NL-B42, 106, and others, University of Pennsylvania, June 30, 1945. Div. 11-101-M9
25. *Progress Report,* R. N. Pease, OSRD 4898.
26. *Literature Survey on the Estimation of Small Amounts of Hydrocarbons in Air: The Importance of These Compounds in the Rectification of Air,* William R. James, Jr. Div. 11-105.1-M2
27. *Estimation of Oil Contamination in Air from Compressors of Portable Air Rectification Units: Report to January 19, 1944,* J. G. Aston, OSRD 3484, Pennsylvania State College, Apr. 14, 1944. Div. 11-105.1-M1

SUPPLEMENTARY

1. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for 1943 to January 31, 1944,* J. H. Rushton, University of Pennsylvania. Div. 11-101-M7
2. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for March 1944,* J. H. Rushton and Barnett F. Dodge, OSRD 3652, University of Pennsylvania, May 19, 1944. Div. 11-101-M7
3. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for April 1944,* J. H. Rushton and W. L. McCabe, OSRD 3760, University of Pennsylvania, June 9, 1944. Div. 11-101-M7
4. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for May 1944,* J. H. Rushton, W. L. McCabe, and Barnett F. Dodge, OSRD 3861, University of Pennsylvania, July 7, 1944. Div. 11-101-M7
5. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for June 1944,* J. H. Rushton, W. L. McCabe, and Barnett F. Dodge, OSRD 3972, University of Pennsylvania, Aug. 2, 1944. Div. 11-101-M7
6. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for July 1944,* J. H. Rushton, Barnett F. Dodge, and W. L. McCabe, OSRD 4142, University of Pennsylvania, Sept. 19, 1944. Div. 11-101-M7
7. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for November 1 to 30, 1944,* J. H. Rushton, W. L. McCabe, and Barnett F. Dodge, OSRD 4516, University of Pennsylvania. Div. 11-101-M7
8. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for December 1 to 31, 1944,* J. H. Rushton, W. L. McCabe, and Barnett F. Dodge, OSRD 4623, University of Pennsylvania. Div. 11-101-M7
9. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for January 1 to 31, 1945,* J. H. Rushton, W. L. McCabe, and Barnett F. Dodge, OSRD 4732, University of Pennsylvania. Div. 11-101-M7
10. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for February 1 to 28, 1945,* J. H. Rushton, W. L. McCabe, and Barnett F. Dodge, OSRD 4879, University of Pennsylvania, Mar. 30, 1945. Div. 11-101-M7

11. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for April 1 to 30, 1945*, W. L. McCabe, OSRD 5153, University of Pennsylvania, May 31, 1945. Div. 11-101-M7
12. *The Investigations Carried Out under Contract OEMsr-232 and New Contract Symbol 904 with Yale University; Monthly Report for March 18, 1942*, Barnett F. Dodge, Yale University, Apr. 19, 1942. Div. 11-101-M2
13. *The Investigations Carried Out under Contract OEMsr-355 with Yale University*, Barnett F. Dodge, Yale University, July 15, 1942. Div. 11-101-M3
14. *Oxygen Generating Equipment, Report to June 30, 1945*, Frederick G. Keyes, OSRD 5329, MIT, July 17, 1945. Div. 11-102-M5
15. *Absorption of CO_2 from Normal Air by Soda Lime*, T. L. Wheeler, Arthur D. Little Company, Inc., Dec. 8, 1943. Div. 11-105.22-M2

Chapter 10

1. *A Colorimetric Method for the Determination of Traces of Carbon Dioxide in Air: Progress Report to February 8, 1943*, Norman A. Spector, OSRD 1426, Yale University, May 17, 1943. Div. 11-105.22-M1
2. *Performance of Heat Insulating Materials at Low Temperatures*, John B. Dwyer, Yale University, Nov. 22, 1943. Div. 11-104.131-M2
3. *Insulating Power of Glass Wool*, Arthur D. Little Co., Apr. 8, 1943. Div. 11-104.131-M1
4. *History of the Development of Heat Exchangers for Low-Pressure Mobile Oxygen Units*, Walter E. Lobo and George T. Skaperdas, M. W. Kellogg Company, Oct. 9, 1943. Div. 11-104.13-M6
5. *Oxygen Plant Development Report to February 28, 1945*, Walter E. Lobo, OSRD 4555, M. W. Kellogg Company, Feb. 28, 1945. Div. 11-102-M4
6. *Methods of Production and Calibration of Combination Vapor Pressure and Gas Dial Thermometers*, Paul Erbguth and J. G. Aston, OSRD 4780, University of Pennsylvania, Jan. 26, 1945. Div. 11-104.2-M5
7. *The Removal of Traces of Acetylene and Other Hydrocarbons from Air*, J. G. Aston and T. A. Geissman, University of Pennsylvania, Mar. 5, 1945. Div. 11-105.23-M1
8. *Final Report of Central Engineering Laboratory, for the Period March 1943 through June 1945*, John A. Goff and Roy W. Banwell, OSRD 5482, University of Pennsylvania, June 30, 1945. Div. 11-101-M9
9. *Combined Oxygen Vapor Pressure and Gas Thermometer: Final Report to January 6, 1944*, J. G. Aston, OSRD 3483, Pennsylvania State College, Apr. 14, 1944. Div. 11-104.2-M3

SUPPLEMENTARY

1. *Combined Oxygen Vapor-Pressure and Gas Thermometers for Use in Temperature Range −320 F to 100 F*, Donald S. Parker and Malcolm L. Sagenkahn, Pennsylvania State College, Sept. 24, 1943. Div. 11-104.2-M1

Chapter 11

1. *Progress Report No. I, Work from October . 1940 to February 15, 1941*, Clifford Hach and Harvey Diehl, Iowa State College, Feb. 17, 1941.
2. *The Effect of Light on the Deoxygenation of Disalicylalethylenediimine Cobalt, Progress Report No. II; Work from February 15 to March 15, 1941*, Clifford Hach and Harvey Diehl, Iowa State College.
3. *Progress Report No. III, Work from March 15, 1941 to Aug. 25, 1941*, Harvey Diehl, Clifford Hach, and G. Harrison, Iowa State College.
4. *Progress Report No. V, Work Done from November 10, 1941 to January 5, 1942*, Harvey Diehl, Clifford Hach, and G. Harrison, Iowa State College, Jan. 8, 1942.
5. *Chelate Compounds for Oxygen Production and Storage*, Melvin Calvin, University of California, Mar. 11, 1942. Div. 11-102.211-M6
6. *Monthly Progress Report, April 15 to May 15, 1942*, Melvin Calvin, University of California.
7. *Chelate Oxygen Compounds: Monthly Progress Report Covering Period from May 15 to June 15, 1942*, Melvin Calvin, W. K. Wilmarth, and others, University of California. Div. 11-102.211-M9
8. *Chelate Oxygen Compounds and Equipment for Their Use, Report No. 378 to August 1, 1942*, Melvin Calvin, OSRD 921, University of California, Sept. 30, 1942. Div. 11-102.211-M10
9. *Chelate Oxygen Compounds and the Mechanism of the Absorption Reaction: Report No. 398 to September 1, 1942*, Melvin Calvin, OSRD 1018, University of California, Oct. 21, 1942. Div. 11-102.211-M12
10. *Chelate Oxygen Compounds: Monthly Progress Report Covering Period from September 1 to October 1, 1942*, Melvin Calvin, W. K. Wilmarth, and others, University of California. Div. 11-102.211-M9
11. *Chelate Oxygen Compounds: Monthly Progress Report Covering Period from October 1 to September 1, 1942*, Melvin Calvin, W. K. Wilmarth, and others, University of California. Div. 11-102.211-M9
12. *Chelate Oxygen Compounds: Monthly Progress Report Covering Period from December 1 to February 1, 1943*, Melvin Calvin, W. K. Wilmarth, and others, University of California. Div. 11-102.211-M9
13. *Chelate Oxygen Compounds: Monthly Progress Report Covering Period from April 1 to June 1, 1943*, Melvin Calvin, W. K. Wilmarth, and others, University of California. Div. 11-102.211-M9
14. *The Activities of the Rumford Research Laboratory in Connection with the Development and Production of Salcomine. Report Covering Period from December 1941 to July 1, 1942*, Karl A. Holst, Rumford Chemical Works, July 6, 1942. Div. 11-102.21
15. *The Progress of the Research on Salcomine and Related Compounds During November 1942*, Karl A. Holst, Rumford Chemical Company, Dec. 11, 1942. Div. 11-102.211-M

16. *The Preparation of 75 Lbs. of 3-Fluoro-Salicylaldehyde and 20 Lbs. of the Active Cobalt Chelate*, Melvin Calvin, Ferguson, and others, University of California, Apr. 1944. Div. 11-102.211-M37
17. *Process for Producing o-Ethavan*, Final Report, O. J. Weinkauff and L. P. Kyrides, Monsanto Chemical Company, July 9, 1943.
18. *Alternative Process for o-Ethavan*, L. P. Kyrides, H. Anthes, and others, Monsanto Chemical Company, Sept. 21, 1943. Div. 11-102.211-M27
19. *Chelate Oxygen Compounds: Monthly Progress Report Covering Period from February 1 to April 1, 1943*, Melvin Calvin, W. K. Wilmarth, and others, University of California. Div. 11-102.211-M9
20. *Chelate Oxygen Compounds: Monthly Progress Report Covering Period from November 1 to December 1, 1942*, Melvin Calvin, W. K. Wilmarth, and others, University of California. Div. 11-102.211-M9
21. *Report, Sc.D. Thesis*, R. L. von Berg, Massachusetts Institute of Technology, April 1944.
22. *The Crystal Structure of the Cobalt Chelates and the Mechanism of the Oxygenation Process*, E. W. Hughes, C. H. Baukelew, and Melvin Calvin, University of California, Mar. 15, 1944. Div. 11-102.211-M34
23. *Properties of Salcomine and Ethomine and the Separation of Atmospheric Oxygen Therewith*, A. M. Smith and W. E. Catterall, OSRD 1539, Massachusetts Institute of Technology, June 25, 1943. Div. 11-102.211-M24
24. *The Development, Properties, and Use of Chelate Compounds for the Production of Oxygen: Report to August 31, 1944*, Melvin Calvin, OSRD 4161, University of California, Sept. 23, 1944. Div. 11-102.211-M41
25. *Catalogue of X-Ray Powder Diagrams of a Number of Pertinent Cobalt Chelate Compounds*, E. W. Hughes and Melvin Calvin, University of California, Apr. 28, 1944. Div. 11-102.211-M38
26. *Preparation of Intermediates for Oxygen-Carrying Chelate Complexes: Report to March 1, 1945*, T. A. Geissman, William G. Young, and others, OSRD 4845, University of California at Los Angeles, Mar. 23, 1945. Div. 11-102.211-M42
27. *Investigation of Oxygen Supply: Progress Report to November 1, 1941*, E. R. Gilliland, OSRD 291, Massachusetts Institute of Technology, Dec. 8, 1941. Div. 11-102.2-M1
28. *Investigation of Oxygen Supply: Report Covering Period to May 31, 1942*, E. R. Gilliland, OSRD 613, Massachusetts Institute of Technology, June 8, 1942. Div. 11-102.212-M3
29. *Regenerative Chemical System for Oxygen Production on Board Aircraft: Report to July 1, 1943*, J. P. ...well and W.E. Catterall, OSRD 1620, Massachusetts Institute of Technology, July 19, 1943. Div. 11-102.21-M6
30. *... Engineering Systems Utilizing Chelate Chemisorbents for Oxygen Production: Report to July ...*, Charles R. Hetherington and W. E. Catterall, OSRD ..., Massachusetts Institute of Technology, July 9, 194.. Div. 11-102.211-M5
31. *Salcomine Deterioration*, C. D. Bell and E. Field, E. I. du Pont de Nemours & Co., Inc., Sept. 30, 1942. Div. 11-102.212-M7
32. *Process Development Work on Salcomine Suspension for Month of September 1942*, L. Squires, E. I. du Pont de Nemours & Co., Oct. 14, 1944.
33. *Study of Salcomine Deterioration*, E. Field and D. M. Smith, E. I. du Pont de Nemours & Co., October 1 to December 12, 1942.
34. *The Preparation and Properties of Mixed Aldehyde Cobalt Derivatives*, Karl A. Holst, Rumford Chemical Co., Jan. 16, 1943. Div. 11-102.211-M11
35. *Development of a Test Unit for Production of Oxygen by a Regenerative Chemical. Supplement Nos. 2, 4, 5, 6 and 7, Progress Reports Covering Period from August 15, 1943 to March 15, 1945*, T. L. Wheeler and Benjamin Fogler, OSRD 3359, Arthur D. Little, Inc., Mar. 7, 1944. Div. 11-102.213-M4
36. *Toxicity Tests on Salcomine and Salcomine Powders*, Julius M. Coon, Howard Glass, and Clarence E. Lushbaugh, OSRD 892, University of Chicago Toxicity Laboratory, Sept. 22, 1942.
37. *Toxicity of Chemical Warfare Agents*, Informal Monthly Progress Report, University of Chicago Toxicity Laboratory, Oct. 10, 1944.
38. *The Effect of Salcomine on Workmen, with Summaries of Physical Examinations*, Arthur D. Little, Inc., Feb. 1, 1944. Div. 11-102.211-M31
39. *The Salcomine Poisoning of T. A. Geissman*, Roy W. Banwell, University of Pennsylvania, January 1944. Div. 11-102.212-M16
40. "Chelate Compounds," T. Tsumabi, *Bulletin of the Chemical Society of Japan*, 13, 1938, pp. 252–260. Div. 11-102.211-M1
41. *Oxygen Plant Development Employing Regenerative Chemicals. Report to March 16, 1945*, Walter E. Lobo and C. Bockius, OSRD 5154, M. W. Kellogg Company and American Machine Defense Corporation, May 31, 1945. Div. 11-102.213-M5
42. *Oxygen-Carrying Metallic Complexes of the Salcomine Type*, T. A. Geissman, OSRD 5927, University of Pennsylvania, June 30, 1945. Div. 11-102.212-M17
43. *The Design of Circulating-Solid Apparatus for the Recovery of Oxygen from the Atmosphere Using the Oxygen Carrier Co-Ox M*, Clifford Hach and Harvey Diehl, Iowa State College, Report I. No. 1 to the NRL and No. 46 to NDRC covering period May 20, 1942 to October 31, 1942.
44. *Oxygen Generating Unit*, from Commanding Officer of USS *Prairie* to Chief, BuShips, O. A. Kneeland, Feb. 15, 1944.
45. *Operating and Maintenance Instructions for Clark 2-Stage 5″x3″x3/4″ Dri-Oxygen Compressor*, Clark Bros. Company.

46. *Instructions for Operation and Maintenance of NDRC Regenerative Oxygen Unit*, Arthur D. Little, Inc., Oct. 1, 1943. Div. 11-102.21-M7

47. *Installation and Trial Test Run of the NDRC Regenerative Oxygen Unit Aboard the U.S.S. Prairie*, C. J. Matthew, A. D. Little, Inc., Oct. 29, 1943.

48. *Production of Oxygen by Regenerative Chemicals*, W. W. Beck, Aug. 19, 1942. Div. 11-102.21-M3

49. *General Description Salcomine Oxygen Navy Unit, Type C-4*, M. W. Kellogg Co., Apr. 20, 1942.

50. *Small Oxygen Plants (Salcomine Process) for Shipboard Installation*, M. W. Kellogg Co., Jan. 19, 1943.

51. *Characteristics of the Oxygen Absorbents Ethomine and Fluorine*, Robert L. von Berg and W. E. Catterall, OSRD 5407, June 30, 1945.

52. *Production of Salcomine and Related Compounds: Report to September 4, 1945*, Karl A. Holst, OSRD 6052, Rumford Chemical Works, Oct. 1, 1945. Div. 11-102.211-M44

53. *Preparation of Intermediates for Oxygen-Carrying Chelate Complexes: Report to March 1, 1945*, T. A. Geissman, William G. Young, and others, OSRD 4845, University of California at Los Angeles, Mar. 23, 1945. Div. 11-101.211-M42

54. *Preparation of Disalicylaltetrafluoroethylenediamine: Monthly Progress Report Covering Period from July 1 to Aug. 4, 1944*, Frederick S. Bacon, University of Pennsylvania, Aug. 7, 1944. Div. 11-102.211-M40

55. *Monthly Progress Report Covering Period June 1 to June 30, 1944: Preparation of Disalicylaltetrafluoroethylenediamine*, Frederick S. Bacon, July 1, 1944.

SUPPLEMENTARY

56. *Report for August 1942*, W. S. Gleeson, American Machine Defense Corp., Sept. 8, 1942.

57. *Kellogg Compressor Project #SSRC-20*, J. D. Wells, American Machine Defense Corp., Oct. 9, 1942.

58. *Progress Report for September 1942*, F. H. Wells, American Machine Defense Corp., Oct. 9, 1942.

59. *Progress Report for October 1942*, F. H. Wells, American Machine Defense Corp., Nov. 6, 1942.

60. *Progress Report for November 1942*, F. H. Wells, American Machine Defense Corp., Dec. 10, 1942.

61. *Progress Report for December 1942*, F. H. Wells, American Machine Defense Corp., Jan. 5, 1943.

62. *Progress Report for January 1943*, F. H. Wells, American Machine Defense Corporation, Feb. 11, 1943.

63. *Progress Report for February 1943*, J. R. Vickery, American Machine Defense Corp., Mar. 8, 1943.

64. *Progress Report, C-2 Salcomine Unit at the Whitlock Mfg. Co., for March 1943*, J. R. Vickery, American Machine Defense Corp., Apr. 5, 1943.

65. *Salcomine Report for Month of June 1942*, E. P. Bartlett, A. G. Weber, and others, E. I. duPont de Nemours & Co., Inc. Div. 11-102.212-M2

66. *Oil-Suspension Salcomine Process as Developed by the Ammonia Department of the duPont Company*, M. W. Kellogg Co., Aug. 5, 1942. Div. 11-1[illegible]12-M6

67. *Salcomine Report for Month of July 1942*, E. P. Bartlett, A. G. Weber, and others, E. I. duPont de Nemours & Co., Inc., Aug. 13, 1942. Div. 11-10[illegible]12-M2

68. *Process Development Work on Salcomine Suspension*, L. Squires, E. I. duPont de Nemours & Co., Sept. 17, 1942.

69. *Manganese Absorbents in the Production of Oxygen from Air*, E. I. duPont de Nemours & Co., Inc., December 1942. Div. 11-102.211-M14

70. *Informed Report on the Progress of the Research on Salcomine and Related Compounds, Dec. 12, 1942 to Feb. 12, 1943*, E. Field and D. M. Smith, E. I. duPont de Nemours & Co.

71. *Informed Report on the Progress of the Research on Salcomine and Related Compounds, Feb. 12, 1943 to Mar. 12, 1943*, D. M. Smith, E. I. duPont de Nemours & Co.

72. *Report on Salcomine*, E. Field, C. D. Bell, J. V. E. Hardy, OSRD 1616, E. I. duPont de Nemours & Co., June 3, 1943.

73. *Salcomine as an Absorbent for Separating Atmospheric Oxygen*, E. Field, C. D. Bell, and J. V. E. Hardy, OSRD 1616, E. I. duPont de Nemours & Co., Inc., July 16, 1943. Div. 11-102.212-M13

74. *Analysis and Degradation Study of Salcomine (Final Report to October 1, 1943)*, OSRD 1951, E. I. duPont de Nemours & Co., Inc., Oct. 25, 1943. Div. 11-102.212-M15

75. *Report IV, August 25, 1941 to November 10, 1941*, Harvey Diehl, Clifford Hach, and G. Harrison, Iowa State College. Div. 11-102.211-M2

76. *Report VI, December 15, 1941 to January 2, 1942*, Clifford Hach, Harvey Diehl, and others, Iowa State College. Div. 11-102.211-M2

77. *Monthly Progress Report*, Harvey Diehl, Iowa State University, Feb. 14, 1942.

78. *Report XII, February 14, 1942 to March 14, 1942*, Clifford Hach, Harvey Diehl, and others, Iowa State College, Mar. 14, 1942. Div. 11-102.211-M2

79. *Development of O_2-Carrying Chemicals, Report XXVI, December 1, 1941 to March 15, 1942*, Harvey Diehl and others, OSRD 574, Iowa State College.

80. *Report XXIII, March 14, 1942 to April 15, 1942*, Clifford Hach, Harvey Diehl, and others, Iowa State College, Apr. 16, 1942. Div. 11-102.211-M2

81. *Report XVII, February 14, 1942 to March 31, 1942*, Clifford Hach, Harvey Diehl, and others, Iowa State College, Apr. 27, 1942. Div. 11-102.211-M2

82. *Report XXI, February 20, 1942 to March 2, 1942*, Clifford Hach, Harvey Diehl, and others, Iowa State College, May 6, 1942. Div. 11-102.211-M2

83. *Report XXVII, March 26, 1942 to May 13, 1942*, Clifford Hach, Harvey Diehl, and others, Iowa State College, May 13, 1942. Div. 11-102.211-[illegible]

84. *Report XXVIII, April 15, 1942 to May 13, 1942*, Clifford Hach, Harvey Diehl, and others, Iowa State College, May 13, 1942. Div. 11-102.211-[illegible]

85. *[illegible] XXXIII, May 13, 1942 to June 15, 1942*, Clif[illegible] Hach, Harvey Diehl, and others, Iowa State Col[illegible] June 17, 1942. Div. 11-102.211-M2

86. *[illegible] XXXII, April 1, 1942 to May 15, 1942*, Clif[illegible] Hach, Harvey Diehl, and others, Iowa State [illegible]ersity, July 14, 1942. Div. 11-102.211-M2

87. *[illegible] XXIV, January 24, 1942 to April 29, 1942*, G. Harrison, Iowa State University, July 20, 1942.

88. *[illegible] XXXIX, June 15, 1942 to July 23, 1942*, Harvey Diehl, Iowa State University, July 23, 1942.

89. *[illegible] XXXVIII, May 13, 1942 to July 24, 1942*, L. Liggett, J. Head, Harvey Diehl, and Melvin Calvin and co-workers, Iowa State University, July 24, 1942.

90. *Report XXXIV, May 20, 1942 to July 23, 1942*, Clifford Hach and Harvey Diehl, Iowa State University, July 25, 1945.

91. *Report XXXV, June 1, 1942 to July 25, 1942*, R. W. Schwandt and Harvey Diehl, Iowa State University, Aug. 5, 1942.

92. *Report XL*, Harvey Diehl, Iowa State University, July 24, 1942 to August 15, 1942.

93. *Development of Oxygen-Carrying Chemicals, Report LXVI*, Iowa State University, April 15, 1942 to September 1, 1942.

94. *Development of Oxygen-Carrying Compounds, Report XVII, April 15, 1942 to September 1, 1942*, Harvey Diehl, OSRD 945, OEMsr-215, Iowa State University, Oct. 16, 1942. Div. 11-102.211-M11

95. *Report XLV, July 11, 1942 to August 24, 1942*, L. Liggett and Harvey Diehl, Iowa State University, Sept. 11, 1942.

96. *Report XLIV, May 1, 1942 to June 1, 1942*, J. Matthews, Jr., and Harvey Diehl, Iowa State University, Sept. 14, 1942.

97. *Report LI, August 15, 1942 to September 15, 1942*, Harvey Diehl, Iowa State University, September 15, 1942.

98. *Oxygen Problem, Summary of Reports from October 20, 1938 to about September 15, 1942*, Clifford Hach, Harvey Diehl, Iowa State University; and other institutions. Div. 11-102.211-M2

99. *Report XLI, April 24, 1942 to May 20, 1942*, J. Head and Harvey Diehl, Iowa State University, Sept. 21, 1942.

100. *Report XXIX, April 17, 1942 to May 15, 1942*, J. Head and Harvey Diehl, Iowa State University, Sept. 21, 1942.

101. *Report XLII, July 22, 1942 to August 21, 1942*, G. Harrison and Harvey Diehl, Iowa State University, Sept. 22, [illegible]

102. *Re[illegible] XXXI, March 15, 1942 to September 7, 1942*, Cli[illegible] Hach, L. Liggett, and Harvey Diehl, Iowa Sta[illegible] [illegible]niversity, Sept. 23, 1942.

103. *R[illegible] XXXVII, June 16, 1942 to August 31, 1942*, R[illegible] [illegible] and Harvey Diehl, Iowa State University, Se[illegible] [illegible], 1942.

104. *R[illegible] [illegible]II, September 15, 1942 to October 15, 1942*, [illegible]

[illegible] Iowa State University.

105. *The [illegible] Apparatus for the [illegible] from the Atmosphere Using the Oxygen Carrier [illegible] May 20, 1942 to October [illegible] 1942*, Clifford Hach and Harvey Diehl, Iowa State University.

106. *Report XLVIII, August 19, 1942 to November 4, 1942*, G. Harrison and Harvey Diehl, Iowa State University, Nov. 4, 1942.

107. *Report LVI, October 15, 1942 to November 16, 1942*, Harvey Diehl, Iowa State University.

108. *Report LV, October 5, 1942 to November 18, 1942*, J. Read and Harvey Diehl, Iowa State University, Dec. 3, 1942.

109. *Report LVIII, November 16, 1942 to December 15, 1942*, Harvey Diehl, Iowa State University.

110. *Oxygen Problem, Report LVII*, Clifford Hach, Ross Curtis, and Harvey Diehl, Iowa State University, Dec. 15, 1942. Div. 11-102.111-M4

111. *Report LIX, October 21, 1942 to November 14, 1942*, L. Liggett and Harvey Diehl, Iowa State University, Jan. 15, 1943.

112. *Report LX, November 14, 1942 to January 1, 1943*, L. Liggett and Harvey Diehl, Iowa State University, Jan. 15, 1943.

113. *Report LI, September 1, 1942 to December 18, 1942*, R. Brouns and Harvey Diehl, Iowa State University, Jan. 20, 1943.

114. *Report LIII, October 26, 1942 to October 29, 1942*, R. Curtis and Harvey Diehl, Iowa State University, Jan. 26, 1943.

115. *Report LXIII, November 19, 1942 to December 29, 1942*, J. Read and Harvey Diehl, Iowa State University, Feb. 5, 1943.

116. *Apparatus for the Determination of the Rate of Oxygenation, Report LXI*, G. Harrison, R. Brouns, and Harvey Diehl, Iowa State University, Feb. 16, 1943. Div. 11-102.21-M4

117. *Report LXV, December 15, 1942 to February 15, 1943*, Harvey Diehl, Iowa State University, Feb. 16, 1943.

118. *Report LIV, October 21, 1942 to December 15, 1942*, G. Harrison and Harvey Diehl, Iowa State University, Feb. 17, 1943.

119. *Report LXII, December 18, 1942 to February 15, 1943*, R. Brouns and Harvey Diehl, Iowa State University, Feb. 19, 1943.

120. *Report LXIV, December 20, 1942 to February 27, 1943*, J. Head and Harvey Diehl, Iowa State University, Mar. 4, 1943.

121. *Report XLVII, Work Intermittently from March 22, 1942 to March 8, 1943*, J. Head and Harvey Diehl, Iowa State University, Mar. 11, 1943.

122. *Report LXIX, February 16, 1943 to March 15, 1943*, Harvey Diehl, Iowa State University, Mar. 15, 1943.

123. *Report LXVI, [illegible] 15, 1943 to March 1, 1943*, R. Brouns and Harvey Diehl, Iowa State University, Mar. [illegible]

124. *Report LXXIV, March 16, 1943 to April 15, 1943.* Harvey Diehl, Iowa State University, Apr. 1, 1943.

125. *Development of Oxygen-Carrying Chemicals. Part III, Progress Report Covering Period from September 1, 1942 to April 20, 1943.* Harvey Diehl, OSRD 1448, Iowa State University, May 24, 1943
Div. 11-102.211-M23

126. *Report LXX, March 1, 1943 to April 10, 1943.* R. Curtis, L. Liggett, and H. Diehl, May 5, 1943.

127. *Report LXXVI, April 15, 1943 to May 14, 1943.* Harvey Diehl, Iowa State University, May 17, 1943

128. *Development of Oxygen-Carrying Chemicals, Fourth Progress Report No. 73 covering period May 20, 1942 to May 20, 1943. A Circulating-Solid Apparatus for the Manufacture of Oxygen.* Clifford Hach and Harvey Diehl, Iowa State University, Oct. 13, 1943
Div. 11-102.211-M28

129. *Report LXXVII, April 20 to May 5, 1943.* L. Liggett, J. Mathews, R. Curtis, and Harvey Diehl, Iowa State University, May 27, 1943.

130. *Development of Oxygen-Carrying Chemicals, Fifth and Final Report No. 79, Covering Period from April 20, 1943 to June 30, 1943.* Harvey Diehl, OSRD 1850, Iowa State University, Oct. 13, 1943
Div. 11-102.211-M29

131. *Development of Test Unit for Production of Oxygen by a Regenerative Chemical, Progress Report for December 1941.* Arthur D. Little, Inc., Feb. 2, 1942
Div. 11-102.211-M5

132. *Report on Development of Manufacturing Process for Salcomine by Rumford Chemical Works (subcontractor to ADL).* Frederick S. Bacon, Arthur D. Little, Inc., Apr. 27, 1942.

133. *Development of Test Unit for Production of Oxygen by a Regenerative Chemical [Report] for April.* Frederick S. Bacon, Arthur D. Little, Inc., May 14, 1942

134. *Development of Test Unit for Production of Oxygen by a Regenerative Chemical [Report] for May, 1942.* Frederick S. Bacon, Arthur D. Little, Inc., June 12, 1942

135. *Development of Test Unit for Production of Oxygen by a Regenerative Chemical [Report] for June, 1942.* Frederick S. Bacon, Arthur D. Little, Inc., July 14, 1942.

136. *Development of Test Unit for Production of Oxygen by a Regenerative Chemical [Report] for August, 1942.* Frederick S. Bacon, Arthur D. Little, Inc., Sept. 11, 1942.

137. *Development of Test Unit for Production of Oxygen by a Regenerative Chemical, Progress Report for January and February, 1942.* T. L. Wheeler and Benjamin Fogler, Arthur D. Little, Inc., Mar. 8, 1943
Div. 11-102.211-M15

138. *Absorption [illegible] Very Small Samples.* Benjamin Fogler, Arthur D. Little, Inc., Mar. 17, 1943.
Div. 11-102.211-M18

139. *Development [illegible] by a Regenerative [illegible] March 1943.* T. L. [illegible] Arthur D. Little, Inc., [illegible]
Div. 11-102.211-M15

140. *Development [illegible] Production of Oxygen by a Regenerative Chemical, Progress Report Covering Period from April 1 through May 15, [illegible]* T. L. Wheeler and Benjamin Fogler, Arthur D. Little, Inc., May 22, 1943.
Div. 11-102.211-M15

141. *Development of Test Unit for Production of Oxygen by a Regenerative Chemical, Progress Report Covering Period May 15, 1943 through June 15, 1943,* T. L. Wheeler and Benjamin Fogler, Arthur D. Little, Inc., June 15, 1943
Div. 11-102.211-M15

142. *Development of Test Unit for Production of Oxygen by a Regenerative Chemical, Progress Report Covering Period from June 15, 1943 through July 15, 1943,* T. L. Wheeler and Benjamin Fogler, Arthur D. Little, Inc., July 21, 1943
Div. 11-102.211-M15

143. *Development of Test Unit for Production of Oxygen by a Regenerative Chemical, Progress Report Covering Period from July 15 to August 15, 1943,* T. L. Wheeler and Benjamin Fogler, Arthur D. Little, Inc., Aug. 19, 1943
Div. 11-102.211-M15

144. *Development of Test Unit for Production of Oxygen by a Regenerative Chemical, Progress Report Covering Period from August 15 to September 20, 1943,* T. L. Wheeler and Benjamin Fogler, Arthur D. Little, Inc., Sept. 27, 1943
Div. 11-102.213-M4

145. *Development of Test Unit for Production of Oxygen by a Regenerative Chemical, Progress Report Covering Period from September 20 through October 10, 1943,* T. L. Wheeler and Benjamin Fogler, Arthur D. Little, Inc., Oct. 20, 1943
Div. 11-102.213-M4

146. *Development of Test Unit for Production of Oxygen by a Regenerative Chemical [Report] through May 15, 1944.* T. L. Wheeler and Benjamin Fogler, Arthur D. Little, Inc., May 22, 1944
Div. 11-102.213-M4

147. *Development of Test Unit for Production of Oxygen by a Regenerative Chemical, Progress Report Covering Period from May 15 through June 15, 1944,* T. L. Wheeler and Benjamin Fogler, Arthur D. Little, Inc., June 16, 1944
Div. 11-102.213-M4

148. *Development of Test Unit for Production of Oxygen by a Regenerative Chemical, Progress Report Covering Period from June 15 through July 15, 1944,* T. L. Wheeler and Benjamin Fogler, Arthur D. Little, Inc., July 20, 1944
Div. 11-102.213-M4

149. *Development of Test Unit for Production of Oxygen by a Regenerative Chemical, Progress Report Covering Period from July 15 through August 15, 1944,* T. H. Wheeler and Benjamin Fogler, Arthur D. Little, Inc., Aug. 25, 1944
Div. 11-102.213-M4

150. *Development of Test Unit for Production of Oxygen by a Regenerative Chemical, Progress Report Covering Period from August 15 through September [illegible] 1944,* T. H. Wheeler and Benjamin Fogler, Arthur D. Little, Inc., Sept. 21, 1944
Div. 11-102.213-M4

151. *Development of Test Unit for Production of Oxygen by a Regenerative Chemical, Progress Report Covering Period from September 15 through October [illegible] 1944,* T. H. Wheeler and Benjamin Fogler, Arthur D. Little, Inc., Oct. 23, 1944
Div. 11-102.213-M4

152. *Development of Test Unit for Production of Oxygen by a Regenerative Chemical, Progress Report Covering Period from October 15 through November 15, 1944,* T. H. Wheeler and Benjamin Fogler, Arthur D. Little, Inc.
Div. 11-102.213-M4

153. *Development of Test Unit for Production of Oxygen by a Regenerative Chemical, Progress Report Covering Period from November 15 through December 15, 1944,* T. H. Wheeler and Benjamin Fogler, Arthur D. Little, Inc.
Div. 11-102.213-M4

154. *Development of Test Unit for Production of Oxygen by a Regenerative Chemical, Progress Report Covering Period from December 15, 1944 through January 15, 1945,* T. H. Wheeler and Benjamin Fogler, Arthur D. Little, Inc.
Div. 11-102.213-M4

155. *Development of Test Unit for Production of Oxygen by a Regenerative Chemical, Progress Report Covering Period from January 15 through February 15, 1945,* T. H. Wheeler and Benjamin Fogler, Arthur D. Little, Inc.
Div. 11-102.213-M4

156. *Development of Test Unit for Production of Oxygen by a Regenerative Chemical, Progress Report Covering Period from February 15 through March 15, 1945,* T. H. Wheeler and Benjamin Fogler, Arthur D. Little, Inc.
Div. 11-102.213-M4

157. *Experimental Finned-Tube Unit, Informal Monthly Progress Report for January 1942,* E. R. Gilliland, R. D. McCrosky, and W. E. Catterall, MIT, January 1942.
Div. 11-102.213-M1

158. *Investigation of Oxygen Supply,* R. D. McCrosky and W. E. Catterall, MIT, February 1942.
Div. 11-102.21-M1

159. *Investigation of Oxygen Supply, Monthly Report for February 1942,* R. D. McCrosky, W. E. Catterall, and others, MIT.
Div. 11-102.21-M2

160. *Investigation of Oxygen Supply, Monthly Report for March 1942,* R. D. McCrosky, W. E. Catterall, and others, MIT.
Div. 11-102.21-M2

161. *Investigation of Oxygen Supply, Monthly Report for April 1942,* R. D. McCrosky, W. E. Catterall, and others, MIT.
Div. 11-102.21-M2

162. *Investigation of Oxygen Supply, Monthly Report for May 1942,* R. D. McCrosky, W. E. Catterall, and others, MIT.
Div. 11-102.21-M2

163. *Investigation of Oxygen Supply, Monthly Report for June 1942,* R. D. McCrosky, W. E. Catterall, and others, MIT.
Div. 11-102.21-M2

164. *Investigation of Oxygen Supply, Monthly Report for June to July 1942,* R. D. McCrosky, W. E. Catterall, and others, MIT.
Div. 11-102.21-M2

165. *Investigation of Oxygen Supply, Monthly Report for July to August 1942,* R. D. McCrosky, W. E. Catterall, and others, MIT.
Div. 11-102.21-M2

166. *Investigation of Oxygen Supply, Monthly Report for September 1942,* R. D. McCrosky, W. E. Catterall, and others, MIT.
Div. 11-102.21-M2

167. *Investigation of Oxygen Supply, Monthly Report for October 1942,* R. D. McCrosky, W. E. Catterall, and others, MIT.
Div. 11-102.21-M2

168. *Investigation of Oxygen Supply, Monthly Report for November 1942,* R. D. McCrosky, W. E. Catterall, and others, MIT.
Div. 11-102.21-M2

169. *Monthly Report for December 1942,* R. D. McCrosky, W. E. Catterall, and others, MIT. Div. 11-102.21-M2

170. *Monthly Report for January 1943,* R. D. McCrosky, W. E. Catterall, and others, MIT. Div. 11-102.21-M2

171. *Monthly Report for February 1943,* R. D. McCrosky, W. E. Catterall, and others, MIT. Div. 11-102.21-M2

172. Letter to E. P. Stevenson, Subject: Standard Apparatus to Be Used in the Evaluation of the Absorption Properties of the Various Compounds Considered in the Oxygen Program, W. E. Catterall, Feb. 3, 1943.

173. *Biological Effects of Carbon Monoxide,* W. E. Catterall, MIT, Feb. 18, 1943.
Div. 11-106.2-M1

174. Letter to Earl P. Stevenson, Subject: Design of Aircraft Unit, W. E. Catterall and J. C. Harper, MIT, Feb. 18, 1943.
Div. 11-102-M5

175. *Monthly Report for March 15, 1943,* R. D. McCrosky, W. E. Catterall, and others, MIT. Div. 11-102.21-M2

176. *Adaptability of Mixed-Base Chelate Compounds to Adiabatic Operation,* Charles R. Hetherington and W. E. Catterall, MIT, Mar. 29, 1943.
Div. 11-102.211-M19

177. *Further Studies on the Deterioration of Ethomine and Salcomine,* W. E. Catterall and A. M. Smith, MIT, Apr. 2, 1943.
Div. 11-102.211-M20

178. *Monthly Report for March 15 to April 15, 1943,* R. D. McCrosky, W. E. Catterall, and others, MIT.
Div. 11-102.21-M2

179. *Regenerative Chemical Field Medical Unit,* W. E. Catterall and Charles R. Hetherington, MIT, May 6, 1943.
Div. 11-102.21-M5

180. *Monthly Report for April 15 to May 15, 1943,* R. D. McCrosky, W. E. Catterall, and others, MIT.
Div. 11-102.21-M2

181. *Monthly Report for May 15 to June 15, 1943,* R. D. McCrosky, W. E. Catterall, and others, MIT.
Div. 11-102.21-M2

182. *Salcomine: Monthly Report Covering Period June 15 to July 15, 1943,* Robert L. von Berg, MIT.
Div. 11-102.212-M12

183. *Characteristics of the Oxygen Absorbents Ethomine and Fluorine, Report to June 30, 1945,* Robert L. von Berg, OSRD 5407, MIT, July 31, 1945.
Div. 11-102.211-M43

184. *The Preparation of o-Ethavan, Monthly Report Covering Period February 10 to April 15, 1943,* O. J. Weinkauff, Monsanto Chemical Company.
Div. 11-102.211-M16

185. *The Preparation of o-Ethavan, Monthly Report Covering Period of April 16 to May 15, 1943,* O. J. Weinkauff, Monsanto Chemical Company.
Div. 11-102.211-M16

186. *Progress of the Research on Salcomine and Related Compounds, Report for September 1942,* Karl A. Holst,

Rumford Chemical Works, Oct. 15, 1942.
Div. 11-102.212-M9

187. *Progress of the Research on Salcomine and Related Compounds, Monthly Report for October 1942*, Karl A. Holst, Rumford Chemical Works, Nov. 12, 1942.
Div. 11-102.211-M10

188. *Progress of the Research on Salcomine and Related Compounds, Monthly Report for January 1943*, Karl A. Holst, Rumford Chemical Works, Feb. 11, 1943.
Div. 11-102.211-M13

189. *Progress of the Research on Salcomine and Related Compounds, Monthly Report for February 1943*, Karl A. Holst, Rumford Chemical Works, Mar. 12, 1943.
Div. 11-102.211-M13

190. *Progress of the Research on Salcomine and Related Compounds, Monthly Report*, Karl A. Holst, Rumford Chemical Works, Apr. 21, 1943. Div. 11-102.211-M13

191. *Progress of the Research on Salcomine and Related Compounds, Monthly Report for May 1943*, Karl A. Holst, Rumford Chemical Works, May 21, 1943.

192. *Monthly Report Covering Period from May 15 to June 15, 1943*, Karl A. Holst, Rumford Chemical Works, June 21, 1943.

193. *The Development of a Method for Preparing Large Quantities of Fluomine, Informal Report Covering Period from February 1 to March 24, 1944*, Karl A. Holst, Rumford Chemical Works.
Div. 11-102.211-M36

194. *Production of Salcomine and Related Compounds*, Karl A. Holst, OSRD 6052, Rumford Chemical Works, Sept. 4, 1945.

195. *Production of Oxygen by the Use of a Regenerative Chemical*, Wendell M. Latimer, OSRD 126, University of California, Aug. 25, 1941. Div. 11-102.211-M3

196. *An Improved Method for the Manufacture of Active Colbalt Salicylaldehydeethylenediamine*, Melvin Calvin, OSRD 403, University of California, Dec. 29, 1941.

197. *Manufacture of Oxygen by Use of Regenerative Chemicals*, Melvin Calvin, OSRD 403, University of California, Dec. 29, 1941. Div. 11-102.211-M5

198. *Informal Monthly Report* in form of Letter to E. P. Stevenson from Melvin Calvin, University of California, Feb. 14, 1942.

199. *Report on Chelate Oxygen Compounds*, Melvin Calvin, University of California, December 1942.

200. *Chelate Compounds for Oxygen Production, Summary Covering Period from February 1 to March 1, 1943*, Melvin Calvin, University of California, March 1943.
Div. 11-102.211-M17

201. *Monthly Report, April 1 to May 1, 1943*, Melvin Calvin, University of California.

202. *Summary Report, June 1 to June 30, 1943*, Melvin Calvin, University of California.

203. *Report for July, 1943*, Melvin Calvin, University of California.

204. *The Laboratory Preparation of 3-Fluorosalicylaldehyde with Suggestions for Pilot Plant Production*, L. Ferguson, R. Holmes, and others, University of California, Oct. 15, 1943.
Div. 11-102 M30

205. *The Manufacture of 50 Lbs. of 3-F-Salicylaldehyde*, Melvin Calvin, University of California, Dec. 9, 1943.
Div. 11-102 M31

206. *The Forms and Methods of Preparation of Cobalt bis-3-Fluorosalicylaldehyde Ethylenediimine*, R. H. Bailes and Melvin Calvin, University of California, Feb. 1, 1944.
Div. 11-102.211-M31

207. *A Report Covering the Preparation of 75 Lbs. of 3-Fluoro-Salicylaldehyde and 20 Lbs. of the Active Cobalt Chelate*, Melvin Calvin, et al., University of California, Apr. 10, 1944.
Div. 11-102.211-M37

208. *Oxygen Carrying Chelate Compounds, Progress Report Covering Period from June 1 to August 31, 1944*, Melvin Calvin, University of California. Div. 11-102.211-M39

209. *Chelate Compounds, Monthly Report*, T. A. Geissman, William G. Young, and others, University of California at Los Angeles, Mar. 15, 1942. Div. 11-102.211-M7

210. *Chelate Compounds, Monthly Report for March 15 to April 15, 1942*, T. A. Geissman, William G. Young, and others, University of California at Los Angeles.
Div. 11-102.211-M8

211. *Chelate Compounds, Monthly Report for April 15 to May 14, 1942*, T. A. Geissman, William G. Young, and others, University of California at Los Angeles.
Div. 11-102.211-M8

212. *Chelate Compounds, Monthly Report for May 15 to June 15, 1942*, T. A. Geissman, William G. Young, and others, University of California at Los Angeles.
Div. 11-102.211-M8

213. *Chelate Compounds, Monthly Report for June 15 to July 15, 1942*, T. A. Geissman, William G. Young, and others, University of California at Los Angeles.
Div. 11-102.211-M8

214. *Chelate Compounds, Monthly Report for July 15 to August 15, 1942*, T. A. Geissman, William G. Young, and others, University of California at Los Angeles.
Div. 11-102.211-M8

215. *Chelate Compounds, Monthly Report for August 15 to September 15, 1942*, T. A. Geissman, William G. Young, and others, University of California at Los Angeles.
Div. 11-102.211-M8

216. *Chelate Compounds, Monthly Report for September 15 to October 15, 1942*, T. A. Geissman, William G. Young, and others, University of California at Los Angeles.
Div. 11-102.211-M8

217. *Chelate Compounds, Monthly Report for October 15 to November 15, 1942*, T. A. Geissman, William G. Young, and others, University of California at Los Angeles.
Div. 11-102.211-M8

218. *Chelate Compounds, Monthly Report for November 15 to December 15, 1942*, T. A. Geissman, William G. Young, and others, University of California at Los Angeles.
Div. 11-102.211-M8

219. *Chelate Compounds, Monthly Report for December 15, 1942 to January 1, 1943*, T. A. Geissman, William G.

Young, and others, University of California at Los Angeles. Div. 11-102.211-M8

220. *Chelate Compounds, Monthly Report for January 1 to February 1, 1943*, T. A. Geissman and William G. Young and others, University of California at Los Angeles.
Div. 11-102.211-M8

221. *Chelate Compounds, Monthly Report for February 1 to March 1, 1943*, T. A. Geissman, William G. Young and others, University of California at Los Angeles.
Div. 11-102.211-M8

222. *Chelate Compounds, Monthly Report for March 1 to April 1, 1943*, T. A. Geissman, William G. Young and others, University of California at Los Angeles.
Div. 11-102.211-M8

223. *Chelate Compounds, Monthly Report for April 1 to May 1, 1943*, T. A. Geissman, William G. Young and others, University of California at Los Angeles.
Div. 11-102.211-M8

224. *Chelate Compounds, Report for the Month of May, 1943*, University of California at Los Angeles.
Div. 11-102.211-M22

225. *Chelate Compounds, Monthly Report for May 1 to June 1, 1943*, T. A. Geissman, William G. Young and others, University of California at Los Angeles.
Div. 11-102.211-M8

226. *Chelate Compounds, Monthly Report for June 1 to July 1, 1943*, T. A. Geissman, William G. Young, and others, University of California at Los Angeles.
Div. 11-102.211-M8

227. *Studies on the Deterioration of Ethomine, Report Covering Period from June 1 to September 1, 1943*, John D. Roberts and R. O. Clinton, University of California at Los Angeles. Div. 11-102.211-M26

228. *Studies on the Deterioration of Salcomine, Report Covering Period August 1 to October 1, 1943*, John D. Roberts and R. O. Clinton, University of California at Los Angeles, October 1943. Div. 11-102.212-M14

Chapter 12

1. *Peroxide Oxygen Generator, Final Report to October 1, 1943*, Walter M. Buehl and John E. Seubert, OSRD 1948, E. I. du Pont de Nemours and Company Inc., Oct. 25, 1943. Div. 11-102.221-M2
2. *Generation of Oxygen from Alkali Peroxides*, S. S. Prentiss, OSRD 1722, Aug. 24, 1943.
Div. 11-102.221-M1
3. *Non-Regenerative Chemical Methods of Producing Oxygen*, S. S. Prentiss, Oct. 6, 1942. Div. 11-102.22-M1
4. *Survey of Oxygen Rebreathers*, Letter of Transmittal and Report, Don M. Yost, Aug. 25, 1942. Div. 11-102.222-M1
5. "Breathing Apparatus for Self-Rescue from Regions of Non-Inhalable Gas," M. Bamberger and F. Bock, *Zeitschrift fur angewandte Chemie*, 17, (1904), p. 1426.
6. *A Pump-Type Nitrogen Eliminator for the Navy High Altitude Rebreather*, Don M. Yost, Don S. Martin, and J. E. Seegmiller, Apr. 13, 1943.
7. *14th Progress Report on Chemical Oxygen Systems*, R. R. Miller, et al., Naval Research Laboratory, 1943.
8. *Test of NRL Chemical Oxygen Unit for Navy Rebreather*, W. Bowen, National Institute of Health, 1944.
9. *A Simplified Rebreather*, S. Goldschmidt, A. Chambers, and G. Millikan, Report to U. S. Navy, Bureau of Aeronautics, Sept. 26, 1944.
10. *A System for Using KOX As a Light, Compact Source of Oxygen for Bailing Out*, W. J. Bowen, National Institute of Health, TED No. 2512, July 1944.
11. *The C-K Oxygen Unit, A Chemical Demand System*, G. A. Millikan, S. Goldschmidt, A. Chambers, and V. Gegallais, Johnson Foundation and Laboratory of Physiology, University of Pennsylvania, CAM No. 443, June 1945.
12. *Report on the Performance of the MSA Navy Type Oxygen Rebreathing Apparatus for Aircraft Use*, A. H. Chambers and S. Goldschmidt, CAM No. 350, Sept. 10, 1944.
13. *Report on Comparison of GOX and KOX Chemicals*, J. N. Stannard, National Institute of Health, May 8, 1943.
14. *Effect of Center Screen Separator on Performance of KOX Canisters*, G. E. Reynolds, W. E. Pricer, J. N. Stannard, National Institute of Health, Report E-36-N-BuAero, Nov. 11, 1943.
15. *The Nitrogen Meter*, J. C. Lilly and T. F. Anderson, CAM Report No. 299, Johnson Foundation, University of Pennsylvania, Feb. 28, 1944.
16. C. E. Berthollet, Mem. Acad. Fran., (1785).
17. *Treatise on Inorganic Chemistry*, J. W. Mellor, Vol. II.
18. J. Scobai, *a. f. Phy. Chem.* 44, (1903), p. 319.
19. E. Blau and R. Weingand, *a.f.Elektroch*, 27 (1921), p. 1.
20. Fry and Otto, *J.Amer.Chem.Soc.* 45 (1923), p.1138.
21. Patents: I. G. Farbenind, A. G. Ger. 566, 780, Feb. 20, 1932; I. G. Farbenind, A. G. Ger. 568, 124, Mar. 13, 1933; Kate Wurster, Ger. 579, 424, June 26, 1933; Marcel Manon, Fr. 758, 827, Jan. 24, 1934; I. G. Farbenind, A. G. Ger. 807, 355, Jan. 11, 1937; I. G. Farbenind, A. G. Ger. 636, 639, Oct. 12, 1936.
22. A. Hloch, *Z. Angew*, 43 (1930), p. 732, also *Chem. Zeit.* 57 (1933), p. 533.
23. Intelligence Report to NRL from Naval Attache in London, Serial 2409, Aug. 26, 1942.
24. *Report 22*, Munitional Supply Laboratories, Maribyrnon, Melbourne, Australia.
25. Wright Field Eng. Report No. 49-660-45H, Dec. 20, 1943.
26. Technical Air Intelligence Report No. 40 OP-NAV-16VT240, John R. Pappenheimer, May 1945.
27. *Report on British Oxygen Candles*, OSRD 1327, A. D. Little Company, Mar. 10, 1943.
28. *NRL Report to Director*, D. S. Burgess, C-JC10, June 7, 1943.
29. Conference, NRL, NDRC, Oldbury Chemical Company, MSA Company, Dec. 17, 1943.
30. *NRL Report to Chief, BuAero*, Ens. W. H. Schechter, C-JC10-1, May 11, 1945.
31. Goodwin and Kalmus, *Phys. Rev.* 28 (1909), p. 10.
32. "Mercury Poisoning," A. M. Fraser, K. I. Melville, and

R. L. Stehle, *J. Ind. Hyg.* 16 (1934), p. 77.

33. *The Layering Economizer*, John R. Pappenheimer and John C. Lilly, CAM Report No. 359, August 1944.
34. *Handbook of Respiratory Data in Aviation*, Nat. Res. Council, CAM 1944.
35. *Measurement of Inspiratory and Expiratory Air Velocities at Altitude*, John R. Pappenheimer and John C. Lilly, Report 208, University of Pennsylvania, Nov. 30, 1943. Div. 11-104.2-M2
36. *Development of Oxygen Candle Apparatus for Use in Aircraft*, John R. Pappenheimer and others, University of Pennsylvania, U.S. Naval Research Laboratory, and other institutions. Div. 11-102.223-M2

SUPPLEMENTARY

1. *Nitrogen Elimination in the Navy High Altitude Rebreather*, Don M. Yost, Northwestern University, Nov. 15, 1943. Div. 11-102.222-M3
2. *Nitrogen Elimination in the High Altitude Rebreather*, Don M. Yost, Don S. Martin, and others, Nov. 15, 1942. Div. 11-102.222-M2
3. *Oxygen Producing KOX Chemical—Specifications for and Availability*, from Director, NRL, to Chief, BuAero, Aug. 17, 1943.
4. *A Study of the Oxides of Potassium and Sodium*, C. A. Kraus and E. F. Whyte, July 6, 1926.
5. *Use of Alkali Oxides in Canisters for Submarine Air Purification*, from Director, NRL, to Chief BuShips, June 26, 1943.
6. *Improved Production of Sodium*, A. G. Arend, Jan. 1, 1943.
7. *Report on Manganese Absorbents in the Production of Oxygen from Air.*

Chapter 13

1. Letter to Earl P. Stevenson, Subject: Low Pressure Oxygen Vaporizer, W. F. Giaque, University of California, Sept. 25, 1943. Div. 11-103.5-M4
2. *Liquid Oxygen Trailer Unit Design, Construction and Operation. Report to July 25, 1944*, W. F. Giauque, OSRD 4141, University of California, Sept. 19, 1944. Div. 11-103.1-M7
3. *Final Report*, John D. Akerman and J. Piccard.
4. *Liquid Oxygen Converter*, W. W. Hay, Ohio Chemical and Manufacturing Co., Sept. 28, 1945.
5. *Problem Related to the Use of Liquid Oxygen and to Design and Operating Characteristics of Liquid Oxygen Converters*, Meeting at University of Pennsylvania, July 13, 1944. Div. 11-103.5-M12
6. *Liquid Oxygen Converter (Akerman), Test of TED-2547* (3rd), from Director of NRL to Chief of BuAero, Feb. 15, 1944. Div. 11-103.5-M13
7. *Report on Akerman Liquid Oxygen Converter Submitted by BuAero, Navy Dept. Washington D.C. on February 16, 1943* (1st), L. J. Briggs, NBS, May 19, 1943.
8. *Liquid Oxygen*, Dept. of Scientific Research and [illegible] ment, Admiralty (File B-4444), March 1944.
9. *Liquid Oxygen Converter (Akerman), Test of* [illegible] *2547*, from Director of NRL to Chief of BuAero, [illegible] 25, 1944.
10. *Oxygen Converters—Test of Dr. J. A. Mathis and* [illegible] *R. Milan's Apparatus*, from Director of NRL to Chi[illegible] of BuAero, Feb. 26, 1943.
11. *Tests of Akerman Oxygen Vaporizer Under Simulated Flight Conditions*, S. S. Prentiss and John R. Pappenheimer, May 4, 1944. Div. 11-103.5-M6
12. *Two Linde Liquid Oxygen Evaporators Submitted by the BuAero, Navy Dept., Washington D.C., on April 7, 1943*, Lyman J. Briggs, National Bureau of Standards, May 18, 1943. Div. 11-103.5-M2
13. *Design and Test of Hand-Operated Liquid Oxygen Pump for Charging High Pressure Cylinders*, T. L. Wheeler and Allen Latham Jr., Arthur D. Little Inc., Sept. 2, 1943. Div. 11-103.2-M1
14. *Problems Related to the Use of Liquid Oxygen and to Design, and Operating Characteristics of Liquid Oxygen Converters*, S. S. Prentiss, University of Pennsylvania, July 1944. Div. 11-103.5-M7
15. *AMAE DDQ, Subcommittee on Oxygen Equipment*, H. Grayson Smith and J. C. Findlay, University of Toronto.
16. *Oxygen Converter, Revised Akerman Apparatus Developed for NDRC*, R. K. West, BuAero, Oct. 26, 1943. Div. 11-103.5-M5
17. "The Use of Liquid Oxygen for High Altitude Flying," John D. Akerman, Reprinted from the *Journal of Aeronautical Science*, **8**, No. 9, July 1941, University of Minnesota, July 1941. Div. 11-103.5-M1
18. *Performance Characteristics of Portable Liquid Oxygen Converters*, V. J. Wulff, U.S. Army Air Forces, Air Technical Service Command, Mar. 15, 1945. Div. 11-103.5-M8
19. *Design Requirements and Test Results on Aircraft Type Liquid Oxygen Converters*, V. J. Wulff, U.S. Army Air Forces, Air Technical Service Command, Mar. 25, 1945. Div. 11-103.5-M9
20. *NDRC NBS Ohio Chemical Conference on Liquid Oxygen Converters*, W. A. Wildhack, National Bureau of Standards, Apr. 9, 1945. Div. 11-103.5-M10
21. *Trip Report—Transportation of Liquid Oxygen*, From Lt. J. P. Layton to BuAero and BuS, Aug. 17, 1943.
22. Patents: U.S. 2260357 Jenner, U.S. 1747366 Heylandt, Re 18476 Heylandt, Re 1773140 Heylandt, Re 18646 Heylandt, Re 1786159 Heylandt, Re 18774 Heylandt, Re 1812954 Heylandt, Fr. 708002 (1931) *L'Oxhydrique Internationale.*
23. *Evaluation of Oxygen Sources—Memo for Director* [illegible] *NRL*, W. H. Sanders, July 14, 1943.
24. *Oxygen Converter Test of the Akerman Apparatus* (1st), Director, NRL, Feb. 8, 1943.
25. *Oxygen Converter Test of Revised Akerman Apparatus* (2nd), Director of NRL to Chief of BuAero, Aug. 4, 1943.

26. *Technical Data Pertaining to Air: Its Liquification and Distillation*, Walter E. Lobo, OSRD 5206, Oct. 6, 1944. (*See Appendix in this volume.*)

Chapter 14

1. *Improvements in Instrument for Measuring the Partial Pressure of Oxygen*, Linus Pauling, Reuben E. Wood, and J. H. Sturdivant, OSRD 779, Report No. 314 to July 10, 1942, California Institute of Technology, Aug. 8, 1942. Div. 11-106.3-M2
2. *A Survey of the Pauling Oxygen Meter Project*, Reuben E. Wood, California Institute of Technology, Sept. 14, 1943. Div. 11-106.3-M5
3. *Performance of Model P Pauling Oxygen Meter in a Flying Airplane*, Reuben E. Wood, California Institute of Technology, Sept. 1, 1943. Div. 11-106.3-M6
4. *The Pauling Oxygen Meter, Report to June 30, 1944*, Reuben E. Wood and David P. Shoemaker, OSRD 4361, California Institute of Technology, Nov. 20, 1944. Div. 11-106.3-M8
5. *Pauling Oxygen Meter*, California Institute of Technology, Feb. 22, 1944. Div. 11-106.3-M7
6. *Oxygen Meters*, Progress Reports covering period from March, 1942 to June 15, 1944, Linus Pauling, OEMsr-326, OEMsr-584, and NDCrc-200, California Institute of Technology, for the following dates: Jan. 14, 1942; Mar. 13, 1942; Apr. 15, 1942; May 12, 1942; June 13, 1942; July 10, 1942; Aug. 11, 1942; Sept. 15, 1942; Oct. 12, 1942; Nov. 11, 1942; Dec. 14, 1942; Feb. 15, 1943; May 15, 1943; June 22, 1943; July 19, 1943; Sept. 15, 1943; Oct. 15, 1943; Nov. 15, 1943; Dec. 15, 1943; Feb. 15, 1944; Mar. 15, 1944; Apr. 15, 1944; June 15, 1944.
7. Final Report, Arnold O. Beckman.
8. *Oxygen Meter, Monthly Reports 1 and 2 Covering Period from November 15 to December 15, 1942*, OEMsr-624, Arnold O. Beckman, California Institute of Technology. Div. 11-106.3-M3
9. *Oxygen Meter, Monthly Reports 1 and 2, Covering Period from November 15, 1942 to December 15, 1942*, Arnold O. Beckman, OEMsr-625, California Institute of Technology. Div. 11-106.3-M4
10. *Methods of Production and Calibration of Combination Vapor Pressure and Gas Dial Thermometers*, Paul Erbguth and J. G. Aston, OSRD 4780, University of Pennsylvania, Jan. 26, 1945. Div. 11-104.2-M5
11. *Combined Oxygen Vapor Pressure and Gas Thermometers for Use in Temperature Range —320°F to 100°F*, Donald S. Parker and Malcolm L. Sagenkahn, Pennsylvania State College, Sept. 24, 1943. Div. 11-104.2-M1
12. *Combined Oxygen Vapor Pressure and Gas Thermometer, Final Report to January 6, 1944*, J. G. Aston, OSRD 3483, Pennsylvania State College, Apr. 14, 1944. Div. 11-104.2-M3
13. *Instrument for Testing Water-Vapor Content and Carbon Monoxide Content in Aviator's Oxygen*, T. L. Wheeler and Gilbert W. King, Arthur D. Little, Inc., Jan. 5, 1944. Div. 11-106.21-M7
14. *Development of Instrument for Measuring Water-Vapor Content in Aviator's Oxygen, Progress Reports covering period from February 1944 to February 1945*, T. L. Wheeler, Gilbert W. King, and Allen Latham, Jr., Arthur D. Little, Inc. Div. 11-106.21-M8
15. *Instrument for Measuring Water-Vapor Content in Aviator's Oxygen, Report to April 11, 1945*, T. L. Wheeler and Howard O. McMahon, OSRD 5151, Arthur D. Little, Inc., May 31, 1945. Div. 11-106.21-M9
16. *Differential Gauge Responsive to Varying Liquid Levels Under Pressure*, Frederick G. Keyes, March 1, 1943.
17. "Determination of Oxygen Concentration by Physical Means," H. Rein, Abstracts from the *Scientific and Technical Press*, No. 106.
18. *Test of A. D. Little Company's Water Vapor Indicator*, National Bureau of Standards to S. S. Prentiss, July 8, 1944.
19. *Test of Oxygen Water-Vapor Indicator, TED No. NBS-2599*, Director of NBS to Chief of BuAero., Jan. 20, 1944.
20. *Operation of the Electrical Water-Vapor Detector*, National Bureau of Standards, May 1, 1943. Div. 11-106.21-M5
21. *Accuracy of the Electrical Method for Determining Water in Compressed Gases*, National Bureau of Standards, June 14, 1943. Div. 11-106.21-M6
22. *A Method for Measuring Water Vapor in Compressed Gases*, National Bureau of Standards, Mar. 20, 1943. Div. 11-106.21-M4
23. Letter to S. S. Prentiss. Subject: Determining Moisture in Oxygen, E. R. Weaver, National Bureau of Standards, Mar. 2, 1943. Div. 11-106.21-M3
24. *A Method for Measuring Water Vapor in Compressed Gases*, National Bureau of Standards, Oct. 9, 1942. Div. 11-106.21-M2
25. *A Method for Measuring Water Vapor in Compressed Gases*, National Bureau of Standards, July 10, 1942. Div. 11-106.21-M1
26. *Performance Tests of Pauling Oxygen Meter, Submarine Model*, Director of NRL to Chief BuS., Mar. 17, 1944.
27. *Bell Laboratories Record*, **17**, No. 2.
28. *Naval Research Laboratory Report No. P 1986*, Jan. 15, 1943.
29. *Preliminary Instruction Sheet for the Operation of MSA Water-Vapor Indicator.*
30. *Instruction for Operation of the Moisture Indicator*, Arthur D. Little, Inc., July 11, 1945. Div. 11-106.21-M10

Chapter 15

1. *Dispersion of Exhaust Gases in Sea Water*, W. H. McAdams, OSRD 1238, MIT, Mar. 4, 1943. Div. 11-106.11-M4
2. *Operation of Diesel Engines on Oxygen*, N. H. Rickles and H. L. Thwaites, OSRD 1425, Standard Oil Development Co., May 17, 1943. Div. 11-106.12-M5
3. *Processes for the Removal of Carbon Dioxide from the Atmosphere of a Submarine*, Allan P. Colburn and Bar-

nett F. Dodge, University of Pennsylvania, Feb. 20, 1944. Div. 11-105.22-M3

4. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen [Report] to December 31, 1944*, J. H. Rushton, W. L. McCabe, and Barnett F. Dodge, OSRD 4623. Div. 11-101-M7

5. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen [Report] to November 30, 1944*, J. H. Rushton, W. L. McCabe, and Barnett F. Dodge, OSRD 4516. Div. 11-101-M7

6. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen [Report] to October 31, 1944*, J. H. Rushton, W. L. McCabe, and Barnett F. Dodge, OSRD 4452. Div. 11-101-M7

7. *Operating Instructions for MIT Model S-Unit for Producing Liquefied Oxygen for Respiratory Use on Submarines and Other Purposes*, Dudley A. Williams, MIT, Mar. 24, 1944. Div. 11-103.3-M5

8. *DuPont Modification of Tessie-duMotay Oxygen Process*, Memo to Walter E. Lobo from J. F. Skelly, W. M. Kellogg Co., Dec. 16, 1942.

Additional Reports of the University of Pennsylvania (OEMsr-934)

(See also the Monthly Progress Reports.)

1. *Monthly Progress Report, March 15, 1943 to January 31, 1944*, J. H. Rushton.

2. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for February 1944*, J. H. Rushton, Barnett F. Dodge, and others, OSRD 3523, University of Pennsylvania. Div. 11-101-M7

3. *Process for the Removal of Carbon Dioxide from the Atmosphere of a Submarine*, A. P. Colburn and Barnett F. Dodge, Feb. 20, 1944.

4. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report*, J. H. Rushton, Barnett F. Dodge, and others, OSRD 3652, University of Pennsylvania. Div. 11-101-M7

5. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for April 1944*, J. H. Rushton, Barnett F. Dodge, and others, OSRD 3760, University of Pennsylvania. Div. 11-101-M7

6. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for May 1944*, J. H. Rushton, Barnett F. Dodge, and others, OSRD 3861, University of Pennsylvania. Div. 11-101-M7

7. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for June 1944*, J. H. Rushton, Barnett F. Dodge, and others, OSRD 972, University of Pennsylvania. Div. 11-101-M7

10. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for July 1944*, J. H. Rushton, Barnett F. Dodge, and others, OSRD 4142, University of Pennsylvania. Div. 11-101-M7

11. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for August 1944*, J. H. Rushton, Barnett F. Dodge, and others, University of Pennsylvania. Div. 11-101-M7

12. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for October 1944*, J. H. Rushton, Barnett F. Dodge, and others, OSRD 4201, University of Pennsylvania. Div. 11-101-M7

13. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for November 1944*, J. H. Rushton, Barnett F. Dodge, and others, OSRD 4302, University of Pennsylvania. Div. 11-101-M7

14. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for December 30, 1944*, J. H. Rushton, Barnett F. Dodge, and others, OSRD 4516, University of Pennsylvania. Div. 11-101-M7

15. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for January 31, 1945*, J. H. Rushton, Barnett F. Dodge, and others, OSRD 4623, University of Pennsylvania. Div. 11-101-M7

16. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for January 31, 1945*, J. H. Rushton, Barnett F. Dodge, and others, OSRD 4732, University of Pennsylvania. Div. 11-101-M7

19. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for May 30, 1945*, J. H. Rushton, Barnett F. Dodge, and others, OSRD 4879, University of Pennsylvania. Div. 11-101-M7

20. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for April 30, 1945*, J. H. Rushton, Barnett F. Dodge, and others, OSRD 5040, University of Pennsylvania. Div. 11-101-M7

21. *Central Engineering Laboratory, NDRC, Section 11.1, Oxygen Monthly Progress Report for May 31, 1945*, W. L. McCabe, OSRD 5153, University of Pennsylvania.

Additional Reports of the Massachusetts Institute of Technology (OEMsr-122 and NDCrc-82)

1. *Experimental Study of Disposal of Exhaust Gases from Internal Combustion Engines on Naval Vessels, Report to May 1, 1941*, James B. Conant, W. H. McAdams, MIT, June 6, 1941. Div. 11-106.11-M1

2. *Monthly Progress Report*, W. H. McAdams, Dec. 20, 1941.

3. *Monthly Progress Report*, W. H. McAdams, Jan. 15, 1942.

4. *Disposal of Engine Exhaust Gases, Quarterly Report Nov. 1, 1941 to Feb. 1, 1942*, W. H. McAdams.

5. *Monthly Progress Report for Work Ending February 15, 1942*, W. H. McAdams.

6. *Monthly Progress Report for February 15 to March 15, 1942*, W. H. McAdams, Mar. 14, 1942.

7. *Monthly Progress Report Covering Period March 15 to April 15, 1942*, W. H. McAdams, Apr. 14, 1942.

8. *Disposal of Engine Exhaust Gases, Quarterly Report for the Period February 1, 1942, to May 1, 1942*, W. H. McAdams, MIT, May 1942. Div. 11-106.11-M

10. *Monthly Progress Report, May 15 to June 15, 1942*, W. H. McAdams.

11. *Monthly Progress Report Covering Period June 15 to July 15, 1942*, W. H. McAdams, July 15, 1942.

12. *Quarterly Report*, W. H. McAdams, July 29, 1942.

13. *Monthly Progress Report Covering Period July 15 to August 15, 1942*, W. H. McAdams, Aug. 12, 1942.

14. *Monthly Progress Report, Disposal of Exhaust Gases*, W. H. McAdams, Sept. 15, 1942.

15. *Disposal of Exhaust Gases*, Memo to E. P. Stevenson from W. H. McAdams, Oct. 27, 1942.

16. *Disposal of Exhaust Gases*, Memo to E. P. Stevenson from W. H. McAdams, Nov. 2, 1942.

Additional Reports of the Standard Oil Development Company (NDCrc-90)

1. Letter to Dr. T. K. Sherwood, Subject, Special Engine Problem, W. J. Sweeney, Standard Oil Development Company, Nov. 27, 1940. Div. 11-106.12-M1

2. *Report on Engine Tests with Chemical Source of Oxygen*, Serial No. 60, W. J. Sweeney, July 21, 1941.

3. *5th Progress Report, Special Engine Project No. 41*, H. L. Leland, W. W. Manville, G. H. Cloud, Standard Oil Development Company, Oct. 27, 1941. Div. 11-106.12-M2

4. *6th Progress Report for Period October 15 to December 2, 1941.*

5. *Special Engine Project No. 41 for Period December 1940 to December 1941, Formal Report*, W. J. Sweeney, Dec. 23, 1941.

6. *Special Engine Project No. 41, Informal Progress Report*, G. H. Cloud, N. H. Rickles, and H. L. Thwaites, Jan. 20, 1942.

7. Appendix to Report of Oxygen Conference, Tuesday, January 27, 1942, MIT, Feb. 9, 1942. Div. 11-106.12-M4

8. *7th Progress Report*, G. H. Cloud, N. H. Rickles, and H. L. Thwaites, Feb. 16, 1942.

9. *8th Progress Report*, N. H. Rickles and H. L. Thwaites, Mar. 18, 1942.

10. *Special Engine Project No. 41—Von Seggern Engine*, G. H. Cloud, Mar. 19, 1942.

11. *Report on Operation of Diesel Engines on Oxygen, OSRD 614, December 2, 1941 to April 16, 1942*, G. H. Cloud, N. H. Rickles, and H. L. Thwaites.

12. *8th Progress Report*, G. H. Cloud, N. H. Rickles, and H. L. Thwaites, Apr. 18, 1942.

13. *Informal Progress Report*, G. H. Cloud, N. H. Rickles, and H. L. Thwaites, Apr. 18, 1942.

14. *10th Progress Report*, June 15, 1942.

15. *11th Progress Report*, G. H. Cloud, N. H. Rickles, and H. L. Thwaites, July 15, 1942.

16. *12th Progress Report*, Aug. 27, 1942.

17. *Special Engine Project #41, 13th Progress Report*, W. J. Sweeney, Sept. 18, 1942.

SUPPLEMENTARY

1. *Maintaining a Normal Breathing Atmosphere in a Submarine*, Research Memorandum 2-44 from Navy Bureau of Ships, Mar. 21, 1944.

2. *Air Purification in Submarines:* (1) Minutes of meeting held August 12, 1943, and (2) paper dated October 12, 1943, Northways, London.

3. *Submarine Propulsion Committee, Minutes of First Meeting Held at Admiralty*, Dec. 1, 1936.

4. *Closed Cycle Operating Characteristics of a Diesel Engine*, Navy Dept. Report, Naval Research Laboratory Report O-2205, L. F. Campbell, W. E. Whybrew, and W. H. Sanders, December 1943.

MICROFILMED BUT NOT IN BIBLIOGRAPHY

[Trailer Unit for Producing Oxygen] Contract NDCrc-206 with Air Reduction Company, Progress Report for August 1942, Wolcott Dennis, Air Reduction Company, Inc., August 1942. Div. 11-102-M2

Oxygen Project, Frederick G. Keyes, NDCrc-182, Special Report 4, MIT, Apr. 15, 1942. Div. 11-102.1-M3

Skid Mounted Oxygen Plant Designed and Built by the Research Laboratory of the Air Reduction Company, Inc., Stamford, Connecticut, Wolcott Dennis, Air Reduction Company, Inc., June 15, 1943. Div. 11-102.12-M3

The Design and Building of Two Sizes of Turbo Expanders, OSRD 6670, The Sharples Corporation, May 24, 1946. Div. 11-102.13-M4

Salcomine, Brief Summaries of Investigations Covering Period from June 1942 to March 12, 1943, E. P. Bartlett, A. G. Weber, and others, E. I. du Pont de Nemours and Company, Inc. Div. 11-102.212-M2

Investigation of Oxygen Supply, Monthly Reports Covering Period from July 1942 to August 31, 1942, W. E. Catterall, A. M. Smith, and others, Massachusetts Institute of Technology. Div. 11-102.212-M4

A Re-Evaluation of the Toxicity of Salcomine, Excerpt from NDRC Informal Monthly Progress Report, No. 9-4-1-21, Oct. 10, 1944. Div. 11-102.212-M18

The Lobo Unit, Reports for the months of August, October, and November 1942, F. H. Wells and W. S. Gleeson, American Machine Defense Corporation. Div. 11-102.213-M2

Oxygen Equipment [Development under] Contract No. OEMsr-409, Monthly Report for December 1942, F. H. Wells, American Machine Defense Corporation, Jan. 5, 1943. Div. 11-102.213-M3

Stability and Concentration of Hydrogen Peroxide, Frederick G. Keyes, W. C. Schumb, and D. B. Broughton, OSRD 5385, OEMsr-1453, MIT, Aug. 1, 1945 Div. 11-102.221-M3

Hydrogen Peroxide, H. S. Gardner and T. K. Sherwood, OSRD 5448, OEMsr-1453, MIT, Aug. 17, 1945. Div. 11-102.221-M4

Laboratory Study of the Possibilities of Commercial Synthesis of Hydrogen Peroxide by Electrical and Photochemical Methods, W. H. Rodebush, C. R. Keizer, and others, OSRD 6644, OEMsr-1452, University of Illinois, Mar. 25, 1946. Div. 11-102.221-M5

Chlorate Oxygen Candles, S. S. Prentiss, Oldbury Chemical Company, Dec. 17, 1943. Div. 11-102.223-M1

The Liquid Oxygen Problem, Report Covering Period from May 1 to June 30, 1941, by W. F. Giauque, June 1941. Div. 11-103.1-M1

Shipboard Oxygen Liquid Unit, Wolcott Dennis and W. G. Fogg, Report 1826, NDCrc-206, Air Reduction Company Inc., June 1, 1942. Div. 11-103.3-M1

Liquid Oxygen Pump, J. P. Layton, BuAero Project 97/43, U.S. Naval Engineering Experiment Station, Annapolis, Maryland, Aug. 17, 1943. Div. 11-103.5-M3

Akerman-Piccard Liquid Oxygen Converter, John D. Akerman and Jean F. Piccard, OEMsr-364, University of Minnesota, June 12, 1945. Div. 11-103.5-M11

Letter to Walter E. Lobo, Subject: Rectification Problems, J. G. Aston, Pennsylvania State College, Jan. 4, 1942 Div. 11-104.11-M1

Full Scale Studies of the Efficiency of Packed Col[illegible]s in Air Rectification (Low Pressure System) in Colla[illegible]tion with the M. W. Kellogg Company, Monthly Repor[illegible] the Period Ending June 30, 1942, J. G. Aston, Penn[illegible]vania State College, July 15, 1942. Div. 11-10[illegible]2-M2

Tests of Performance of an 8-Inch Portable Unit [illegible]umn for Air Rectification, Progress Reports for Period J[illegible] and August 1942, J. G. Aston and others, Pennsylvania State College. Div. 11-104.12-M1

Tests of Performance of Portable Unit Columns for Air Rectification, Progress Reports for Period from August 1942 to September 1943, J. G. Aston, Charles Brouse, and others, Pennsylvania State College Div. 11-104.12-M3

Analysis of the Ammonium Hydroxide Ammonium Chloride Copper Method for High Oxygen Content Gases Contaminated with Argon or Nitrogen, D. C. Reams, Jr., Central Engineering Laboratory, June 1, 1944. Div. 11-104.2-M4

Dispersers, Monthly Progress Report for Period from November 15 to December 15, 1941, W. H. McAdams, MIT, Dec. 20, 1941. Div. 11-106.111-M1

Water Injection Disperser, Monthly Progress Report Covering Period from January 15 to February 15, 1942, W. H. Adams, NDCrc-82, MIT, February 1942. Div. 11-106.111-M2

Carbon Dioxide Gas, Monthly Progress Report Covering Period from February 15 to March 15, 1942, W. H. McAdams, OEMsr-122, MIT, Mar. 14, 1942 Div. 11-106.111-M3

Carbon Dioxide Gas, Monthly Progress Report Covering Period from March 15 to April 15, 1942, W. H. McAdams, OEMsr-122, MIT, Apr. 14, 1942 Div. 11-106.111-M4

Two Stage Water Injection Type Gas Disperser, Monthly Progress Report Covering Period from May 15 to June 15, 1942, W. H. McAdams, OEMsr-122, MIT, June 15, 1942 Div. 11-106.111-M5

Dispersion-Absorption Runs, Monthly Progress Report Covering Period from June 15 to July 15, 1942, W. H. McAdams, OEMsr-122, MIT, July 15, 1942. Div. 11-106.111-M6

Two-Stage Water Injection Dispersers, Quarterly Report for Period Ending July 31, 1942, W. H. McAdams, OEMsr-122, MIT, July 29, 1942. Div. 11-106.111-M7

Two-Stage Dispersers, Monthly Progress Report Covering Period from July 15 to August 15, 1942, W. H. McAdams, OEMsr-122, MIT, Aug. 12, 1942. Div. 11-106.111-M8

Letter to T. K. Sherwood, Subject: Special Submarine En[illegible]gine Problem, W. J. Sweeney, Standard Oil Developm[illegible] Company, Nov. 27, 1940. Div. 11-106.12-[illegible]

Special Engine Project 41, Fifth Progress Report, G. [illegible] Cloud, H. L. Leland, and W. W. Manville, NDCr[illegible], Standard Oil Development Company, Oct. 27, 1941. Div. 11-106.12-[illegible]

Special Engine Project 41, Monthly Reports Covering P[illegible]iod from December 2, 1941 to September 15, 1942, G. [illegible] Cloud, N. H. Rickles, and H. L. Thwaites, NDCrc-90, Stan[illegible]ard Oil Development Company Div. 11-106.12-[illegible]

Appendix to Report of Oxygen Conference, Tuesday, Jan[illegible]ary 27, 1942, W. J. Sweeney, MIT, Feb. 9, 1942. Div. 11-106.12-[illegible]

OSRD APPOINTEES

DIVISION 11

Division 11 was organized on December 9, 1942, when former Division B of the NDRC was broken up into four new Divisions—8, 9, 10, and 11—known as the Chemical Divisions. Former Division B was under the chairmanship of Roger Adams and had ten sections, each of which had one or more subsections. Division 11 was made up of Sections B-7, B-8, part of B-9, and B-10 (together with subsections B-7-b, B-7-d, B-7-e, B-8-a, B-8-b, B-8-c, B-8-d, B-8-e, B-8-f, B-9-a, and B-9-d) of former Division B. Subsections B-9-b and B-9-e of Section B-9 later became Division 19.

The list which appears below therefore shows essentially the organization since December 9, 1942. Although many changes were made during the years 1943–1945, the names of all appointees who held appointments to Division 11 at any time during this period have been included. In addition the names of men who held appointments in the sections and subsections of former Division B but who did not have appointments to Division 11 following the reorganization have been included so as to give a complete picture of the organization since the beginning of the work under NDRC.

Section 11.1 comprises Subsection B-7-b of former Division B.

Division Chiefs

R. P. Russell
E. P. Stevenson
H. M. Chadwell

Division Technical Aide

D. Churchill, Jr.

Division Members

D. Churchill, Jr.
E. R. Gilliland
H. C. Hottel
H. F. Johnstone
W. K. Lewis
J. H. Rushton
R. P. Russell
T. K. Sherwood
E. P. Stevenson

SECTION 1

Section Chiefs

E. P. Stevenson
J. H. Rushton

Section Technical Aides

D. Babcock
W. W. Beck
S. C. Collins
D. R. Dewey
C. C. Furnas
H. B. Goff
S. S. Prentiss
J. H. Rushton

Section Members

T. H. Chilton
B. F. Dodge
C. C. Furnas
E. R. Gilliland
W. R. Hainsworth
F. G. Keyes
W. H. McAdams
F. J. Metzger
W. J. Sweeney

CONTRACT NUMBERS, CONTRACTORS, AND SUBJECT OF CONTRACTS

Contract No.	Name and Address of Contractor	Subject
NDCrc-82	Massachusetts Institute of Technology, Cambridge, Massachusetts	Disposal of exhaust gas from submarines.
NDCrc-90	Standard Oil Development Company, 26 Broadway, New York, N.Y.	Engine performance tests with special fuels.
NDCrc-38	California Institute of Technology, Pasadena, California	Oxygen analyzer.
NDCrc-129	University of California, Berkeley, California	Regenerative oxygen-absorbing compounds (Salcomine).
NDCrc-182	Massachusetts Institute of Technology, Cambridge, Massachusetts	Design, construction, and testing of a pilot plant liquid-oxygen producer.
NDCrc-198	University of California, Berkeley, California	Design, construction, and testing of a mobile liquid oxygen plant utilizing the cascade system.
NDCrc-200	California Institute of Technology, Pasadena, California	Oxygen analyzer.
NDCrc-206	Air Reduction Company, Inc., 60 East 42nd Street, New York, N.Y.	Rectifying column for use in oxygen-generating plants and design and construction of a mobile oxygen unit.
OEMsr-4	Massachusetts Institute of Technology, Cambridge, Massachusetts	Apparatus for generating oxygen with regenerative oxygen-absorbing compounds.
OEMsr-122	Massachusetts Institute of Technology, Cambridge, Massachusetts	Disposal of exhaust gas from submarines.
OEMsr-215	Iowa State College, Ames, Iowa	Regenerative oxygen-absorbing compounds.
OEMsr-232	Yale University, New Haven, Connecticut	Experimental study of devices for oxygen production.
OEMsr-269	Arthur D. Little, Inc., 30 Memorial Drive, Cambridge 42, Mass.	Construction and testing of miscellaneous types of apparatus for producing and handling oxygen.
OEMsr-279	University of California, Berkeley, California	Regenerative oxygen-absorbing compounds.
OEMsr-326	California Institute of Technology, Pasadena, California	Improvements in Pauling meter.
OEMsr-355	Yale University, New Haven, Connecticut	Testing of apparatus for oxygen production.
OEMsr-364	University of Minnesota, Minneapolis, Minnesota	Design and construction of liquid oxygen vaporizers.
OEMsr-365	The M. W. Kellogg Company, 225 Broadway, New York, N.Y.	Design and engineering of oxygen-producing units.
OEMsr-370	Clark Brothers Company, Inc. Olean, New York	Construction of mobile oxygen units and apparatus therefor.
OEMsr-395	University of California, Los Angeles, California	Synthesis and study of regenerative oxygen-absorbing compounds.
OEMsr-454	The Linde Air Products Company 5502-5524 Second Ave., Brooklyn, N.Y.	Study and analysis of oxygen cycles.
OEMsr-499	American Machine and Foundry Company, 30 East 42nd Street, New York, N.Y.	Development and construction of apparatus for producing oxygen from Salcomine.
OEMsr-530	Independent Engineering Company, O'Fallon, Illinois	Development and construction of mobile oxygen-producing units utilizing Salcomine.
OEMsr-584	California Institute of Technology, Pasadena, California	Development of oxygen partial-pressure indicators for use on submarine and aircraft.
OEMsr-604	E. I. du Pont de Nemours and Company, Wilmington, Delaware	Investigation of methods of producing oxygen from Salcomine suspended in liquid media.
OEMsr-605	Rumford Chemical Works, Rumford, Rhode Island	Manufacture of large batches of Salcomine.

CONTRACT NUMBERS, CONTRACTORS, AND SUBJECT OF CONTRACTS (*continued*)

Contract No.	Name and Address of Contractor	Subject
OEMsr-624	A. O. Beckman, South Pasadena, California	Manufacture of Pauling meters on orders approved by OSRD.
OEMsr-625	A. O. Beckman, South Pasadena, California	Development of Pauling meters for use on submarines.
OEMsr-654	J. F. Pritchard and Company, 2200 Fidelity Bank Building, Kansas City, Missouri	Construction of equipment for large liquid-oxygen pilot plants.
OEMsr-666	The Sharples Corporation, 23rd and Westmoreland Streets, Philadelphia, Pennsylvania	Development and construction of turbo expanders.
OEMsr-685	Pennsylvania State College, State College, Pennsylvania	Testing of oxygen-producing equipment.
OEMsr-798	Elliott Company, Jeannette, Pennsylvania	Design and development of turbo compressors and expanders.
OEMsr-863	E. I. du Pont de Nemours and Company, Wilmington, Delaware	Design and construction of generators for producing oxygen from alkali peroxides.
OEMsr-903	Monsanto Chemical Company, St. Louis, Missouri	Development of method for making ortho-ethavan.
OEMsr-914	Servel, Inc., 51 East 42nd Street, New York, N.Y.	Construction of small liquid-oxygen units.
OEMsr-934	University of Pennsylvania, Philadelphia, Pennsylvania	Central laboratory for the oxygen program.

SERVICE PROJECTS

The projects listed below were transmitted to the Executive Secretary, NDRC, from the War or Navy Department through either the War Department Liaison Officer for NDRC or the Office of Research and Inventions (formerly the Coordinator of Research and Development), Navy Department.

Service Project No.	Subject
	Army Projects
AC-12	The Manufacture of Oxygen while in Flight for Use of the Combat Crew.
AC-32	Lubricants for Use with Oxygen at High Pressure.
CE-29	Field Generation of Oxygen.
	Navy Projects
NA-106	Development of Oxygen Breathing Equipment and Associated Apparatus.
NA-111	Portable Unit for Supplying Oxygen.
NA-138	Compact Apparatus for Determining Suitability of Oxygen for Use in Aircraft at High Altitude, Development of
NL-B1(f)	Development of an Instrument for the Measurement of Oxygen Partial Pressures
NL-B6	Operation of Submarine Engines while Submerged
NL-B6(b)	Engine Tests on Oxygen-Supplying Chemicals; Oxygen and Oxygen-Containing Fuels.
NL-B6(c)	Absorption of Exhaust Gases.
NL-B6(d)	Equipment for Manufacture of Liquid Oxygen
NL-B42	Development of Chemicals and Apparatus for Regenerative Production of Oxygen
NS-115	Liquid Oxygen Plant.
NS-116	Portable Unit for Producing Oxygen for Welding and Cutting and Breathing Oxygen Aboard Aircraft
NS-117	Oxygen-Producing Apparatus for Repair Ship Installation
NS-226	Submarine Air Conditioning with Liquid Oxygen.

INDEX

The subject indexes of all STR volumes are combined in a master index printed in a separate volume. For access to the index volume consult the Army or Navy Agency listed on the reverse of the half-title page.

REEL – C

1264

A.T.I.

30819

TITLE: Improved Equipment for Oxygen Production Vol. 1 AUTHOR(S): Prentiss, S. S.; Rushton, J. H. ORIGINATING AGENCY: Office of Scientific Research and Development, NDRC, Div. 11 PUBLISHED BY: (Same)	ATI- 30819 REVISION (None) ORIG. AGENCY NO. (None) PUBLISHING AGENCY NO. (None)

DATE	DOC. CLASS.	COUNTRY	LANGUAGE	PAGES	ILLUSTRATIONS
1946	Unclass.	U.S.	Eng.	435	photos, tables, diagrs, graph

ABSTRACT:

The process of generating and using oxygen, as applied to military procedure, has been developed by the Chemical Engineering Division (NDRC). Three categories of this process are outlined, i. e., the development of compact, lightweight, portable units for separating oxygen from air; the development of equipment for supplying oxygen for specialized uses, such as aircraft breathing, and of instruments for testing the oxygen intended for the specialized uses; and the generation of oxygen aboard submarines for use as a secondary fuel; and the operation of internal combustion engines while the vessels are submerged. The development of the component parts of several alternative forms of apparatus for generating oxygen and charging cylinders are discussed in great detail.

DISTRIBUTION: Copies of this report obtainable from Air Documents Division; Attn: MCIDXD

DIVISION: Comfortization (23) SECTION: Oxygen Systems (2) ATI SHEET NO.: R-23-2-4	SUBJECT HEADINGS: Equipment, Oxygen (34269.2); Oxygen generating units, Mobile (68727.97); Oxygen generating units, Airborne (68727.95); Oxygen generating units, Shipborne (68727.973); Research - Summary reports (81658.95)